THE UNIVERSITY of EDINBURGH

" STUDIES ON ANHYDRO SALTS "

By

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FOREWORD

This work is an account of two years research in fulfilment of Ph.D. requirements, which has been conducted under the supervision of Prof. E.L.Hirst and Dr. W.H.Stafford.

To Dr. Stafford the author wishes gratefully to acknowledge his kind assistance and guidance, which have made this research a very pleasant experience. Thanks are also due to Miss W.L.Galloway and Mr. A.G. Clark for assistance with some of the spectral work, during their under-graduate course.

J.P.S.

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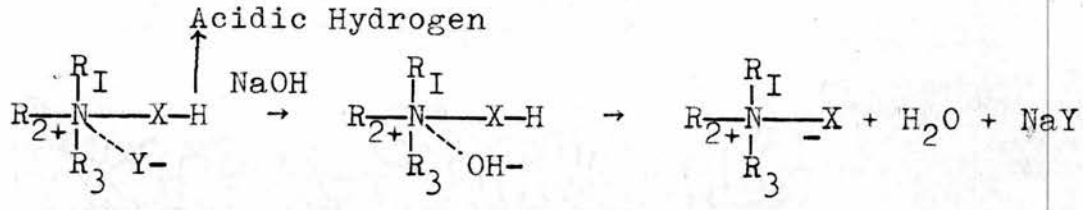
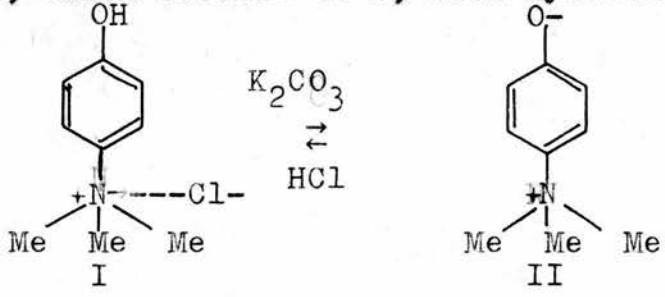
INTRODUCTION

"Anhydro Salts" (Brown and Hammick, J., 1950, 630) are internal salts or betaines, (Pfeiffer, Ber., 1922, 55, 1762) derived from cationic compounds possessing an acidic group, or a group capable of acting as an acid, by the loss of a proton. The process of anhydro salt formation usually involves the treatment of a salt, e.g. a quarternary ammonium compound, with alkali, and, formally at least, appears to result from the dehydration of the hydroxide derived from the cation.



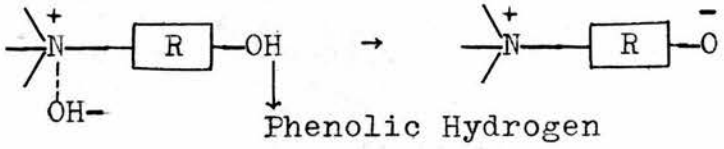
These anhydro salts are basic compounds, and react with acids to give their progenitors, which is the reversal of their mode of formation. For example, the phenolic ammonium chloride, I, when treated with dilute potassium carbonate, liberated the anhydro salt, II, which reverts to I, with hydrochloric acid.



The basic nature of these compounds, led to the use of the name "anhydro base", before the internal

salt like structure was appreciated by Pfeiffer on the basis of Lewis Langmuir's theory of salt character. Anhydro salts, thus come under the head of basic betaines, which originate from a base hydroxide, containing an acidic group, by loss of the elements of water. In the original base, the cationic centre, unlike the amphoteric betaines, bears no hydrogen, which may be lost as a proton, so the stability of the anhydro salt depends, primarily, upon the lack of basicity of the anionic centre; i.e. its inability to acquire or retain a proton. The anhydro salts have been classified into separate groups, according to the acid group, from which the proton is lost during their formation.

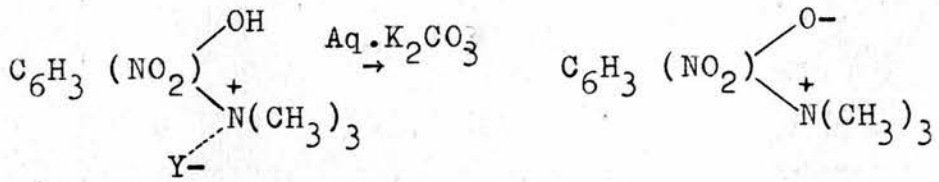
(1) Phenol Betaines:- These betaines, in general are formed by the dehydration of a cationic compound, possessing a phenolic group as the acid group, which loses a proton. The cation in most cases is a quarternary nitrogen, in the form of ammonium, pyridinium, quinolinium or isoquinolinium bases. Their general method of formation could be represented as -



R is any aromatic structure; and the cation, the quarternary nitrogen, may be within or without this

aromatic nucleus.

The first mention of a quarternary ammonium type phenol betaine, Trimethyl nitrophenyl ammonium hydroxide anhydro salt III, was by P. Griess (Ber., 1880, 13, 647). This betaine was

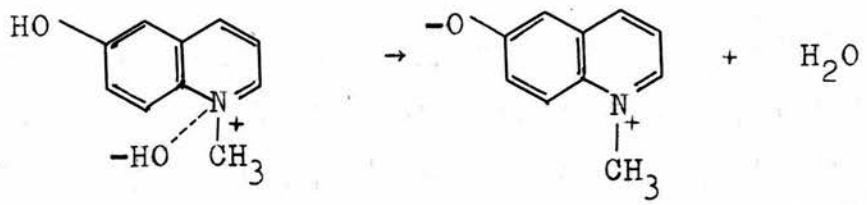


IV III

derived from the quarternary ammonium salt IV, by treatment with silver oxide, silver carbonate or preferably with potassium carbonate solution. The anhydro salt crystallised from boiling water as yellow shining needles or as elongated plates, which did not melt on heating to 200°c. The betaine is readily soluble in boiling water or boiling alcohol, but is sparingly soluble in ether and benzene. The compound is highly basic, and forms salts with acids, from which it is regenerated on treatment with potassium carbonate solution.

The phenol betaines of the pyridinium, quinolinium or isoquinolinium series, have been described by a number of workers, but it was A. Claus who first gave the name "Phenol Betaines" to such compounds, (J. Prakt. Chem., 1891, 43, 505-522) when he first reported the isolation of 6-hydroxy quinoline metho-betaine, V, as a crystalline dihydrate. This he

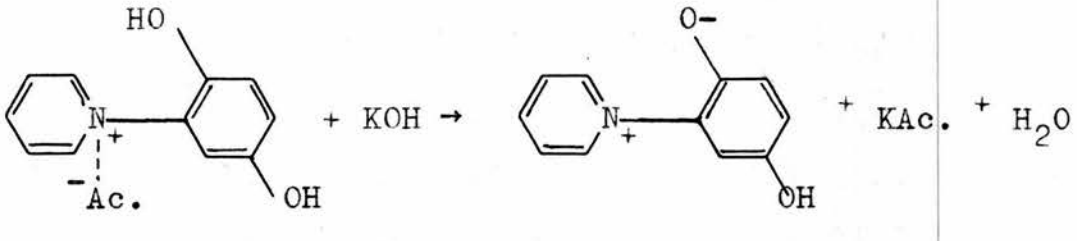
obtained by the dehydration



VI V

of 6-hydroxy quinolinium hydroxide, VI. The yellow betaine on drying gave dark red needles, which rapidly absorbed moisture on exposure to the atmosphere, reverting to the yellow hydrate. The betaine was readily soluble in water, and even more soluble in alcohol, giving a yellow coloured solution. The basicity of this compound was shown by the readiness with which it formed colourless salts with acids., e.g. the carbonate and hydrochloride. From these salts the betaine is regenerated by treatment with silver oxide or silver carbonate, or preferably with aqueous potassium carbonate. Such an alkaline treatment of the quarternary ammonium salt, to generate phenol betaines has been quite commonly used for their preparation.

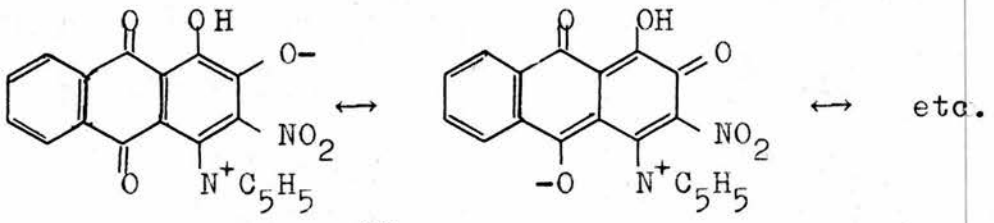
Diels and Kassebart (Annalen, 1937, 530, 51) prepared N - (2:5-dihydroxyphenyl) pyridinium hydroxide anhydro salt VIII by the action of alkali on N - (2:5-dihydroxyphenyl) pyridinium acetate. VII; the latter substance was prepared by treating



VII VIII

p-quinone with pyridine in acetic acid, in a manner analogous to Ortoleva and Stefano's (Gazz, 1901, 31, 256) preparation of the iodide. The anhydro salt crystallised as a strawberry coloured dihydrate from 50% acetonitrile and on drying gave a violet to black substance, analysing correctly for the betaine. The basic nature of this betaine is shown by the readiness with which it formed colourless salts with acids.

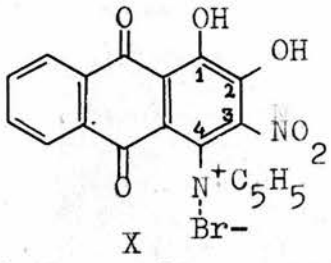
Apart from these strongly basic phenol betaines, weakly basic betaines, have been made which need no treatment with alkali to generate them, as they so readily lose a proton, e.g. 3-nitro alizarin-4-N pyridinium hydroxide anhydro salt IX, made by Barnett and Cook (J., 1922, 1389) by the bromination of 3-nitro alizarin in pyridine solution. The product contained no bromine and was an anhydro salt.



IX

The reaction could be explained by (1) the bromination

in 4- position, followed by (2) the formation of the intermediate, X, with pyridine, which readily transforms into IX, due to the ease with which the hydrogen from the phenolic group in the 2-position is lost, in presence of the weak base, pyridine.

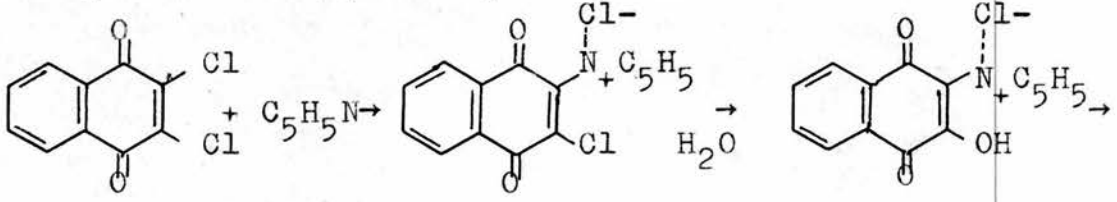


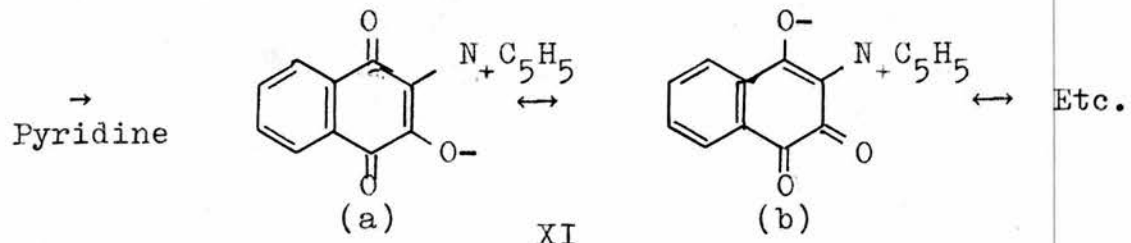
X

→ Pyridine IX

The anhydro salt was soluble in boiling hydrobromic acid, to give a yellow solution, which on cooling deposited the red crystalline dihydrate of the anhydro salt. It is therefore an extremely weak base; the cause of this must be attributed to the various contributing forms, which cause the stabilisation of the anion.

Ullman and Ettisch (Ber., 1921, 54, 261) prepared 2-hydroxy 1:4 naphthoquinone-3-N-pyridinium hydroxide anhydro-salt, XI, by treating 2:3-dichloro-1:4-naphthoquinone with pyridine, as shown.

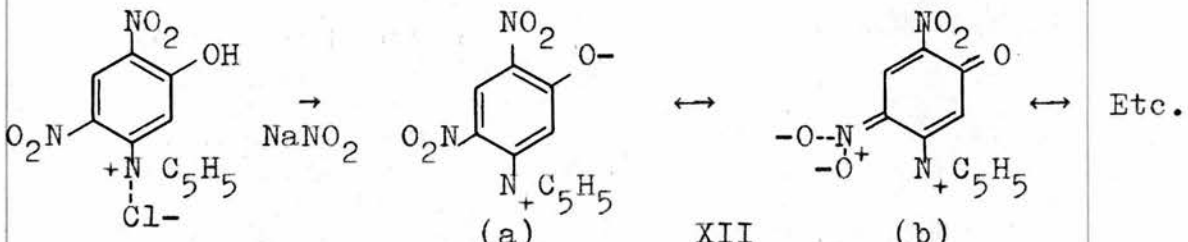




(a) XI (b)

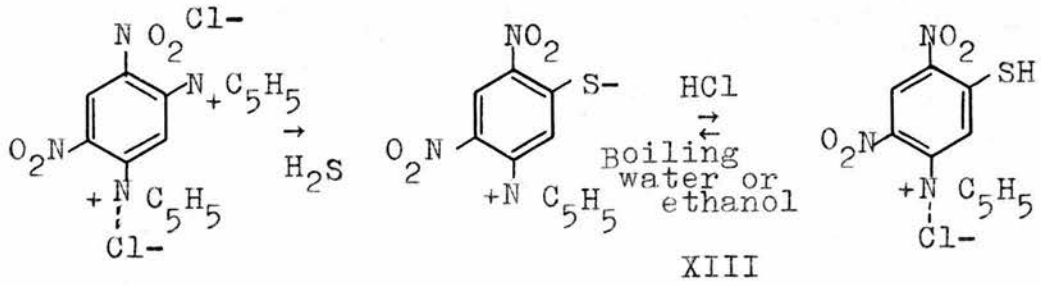
The anhydro salt is soluble in concentrated hydrochloric acid, and crystallises on dilution. It must therefore be weakly basic.

Zincke and Weispfenning (J. Prakt. Chem., 1910, 82, 1) obtained, N-(2:4-dinitro-5-hydroxy phenyl) pyridinium hydroxide anhydro salt XII, by treating N-(2:4-dinitro-5-hydroxyphenyl) pyridinium chloride with a weak base (sodium nitrite). The



anhydro salt is yellow in colour and gives colourless salts with strong acids. It may however be crystallised from glacial acetic acid. This is therefore of intermediate basicity.

Zincke, (J. Prakt. Chem.,1912, 85, 214) isolated a red brown thiophenol betaine XIII, by passing hydrogen sulphide through an aqueous or alcoholic solution of 1:3:4:6-dinitrophenyl-dipyridinium chloride. This with acids, gave colourless salts, from which it could be regenerated by boiling the salt,in water or in ethanol. It is thus weakly basic.



The chief characteristics of these anhydro salts are:-

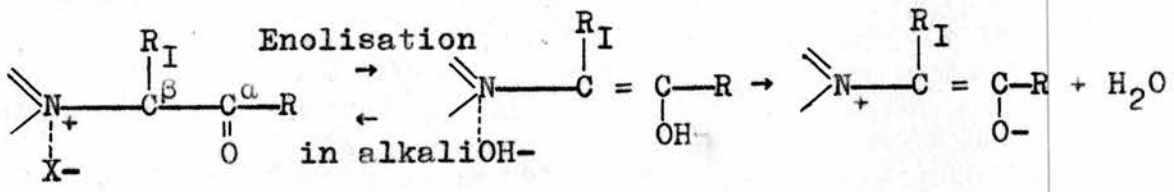
(1) Basicity:- They are either strongly or weakly basic, according to the tendency of the anionic group, to acquire or to lose a proton. The weak basicity of certain compounds, is due to the stability of the anionic group, (viz. the negatively charged oxygen or sulphur) caused by the various mesomeric forms, (polar or covalent) which contribute to the original structure.

(2) Colour:- All the phenol betaines are intensely coloured. In different solvents, they have different colours, which has a bearing on their salt like structure. This feature will be dealt with, in detail, later on.

(3) Hydration:- These anhydro salts have great affinity for the hydroxylic solvents, like water and ethanol; which they tend to retain as the solvents of crystallisation. Dry anhydro salts are very hygroscopic, and readily absorb moisture from the atmosphere. The hydration, is accompanied by change in colour, both in the solid state as well as in solution. The phenol betaines are quite stable, but their stability is enhanced all the more with hydration. This feature of change in colour, and increase in stability on hydration must be attributed to the phenomenon of hydrogen bonding. This shall be discussed in detail later.

Enol-betaines and the $\bar{c}$-Betaines:-

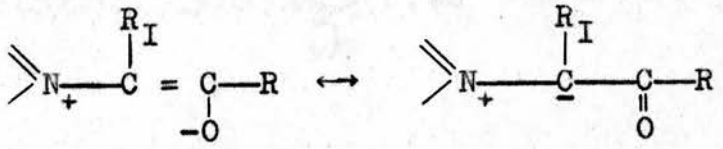
The enol betaines, are the products of reaction with alkali, of a cationic compound (viz. quarternary ammonium, anilinium, pyridinium, quinolinium, or isoquinolinium etc.), containing an enolisable group. The latter although not "acid" is capable of losing a proton. A general representation of such a reaction is:-



R = alkyl or substituted alkyl group.

R_1 = hydrogen, alkyl or acyl group.

Such an enol betaine exists in various mesomeric forms e.g.

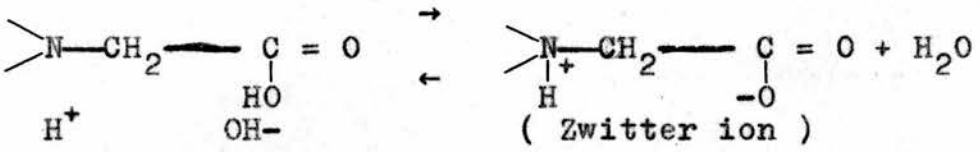


(i) (2)

The possibility of existence of the form (2) is quite feasible, due to the known existence of the carbon anions. As such, the enol betaines are also $\bar{c}$-betaines, whereas a $\bar{c}$-betaine is not essentially an enol betaine, as will be shown later.

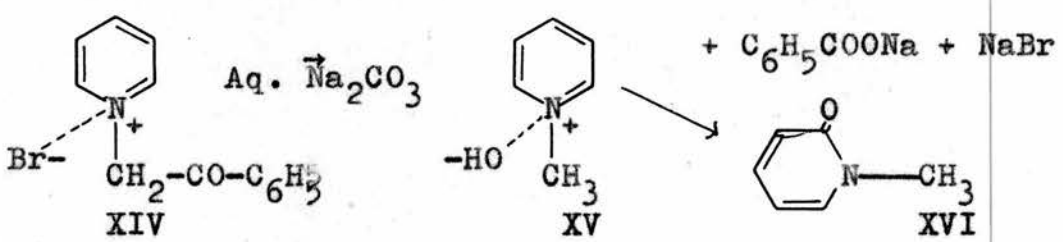
Structurally the enol betaines could be contrasted with the amphoteric betaines, the Zwitter ions afforded

in aqueous solution by the amino-acids of the glycine series. The removal of a proton takes place in both the cases, from the (-OH) group attached to the carbon atom, leaving a betainoid structure.



The preparation of enol betaines was the result of several investigations by a number of chemists. Bamberger (Ber.,1887, 20, 2344) discovered that treatment of phenacyl pyridinium bromide XIV, with alkali, yielded sodium benzoate. This he thought, was due to the decomposition of phenacyl pyridinium bromide by the alkali, to give phenacyl bromide or phenacyl alcohol which reacted further to give benzoic acid.

Zincke (Annalen.,1882, 216, 311), however had shown that the action of alkali on phenacyl bromide or phenacyl alcohol, gives no benzoic acid, so that Bamberger's explanation becomes untenable. Schmidt and Van Arck (British Chem. Abs., 1900, I, 687) reacted phenacyl

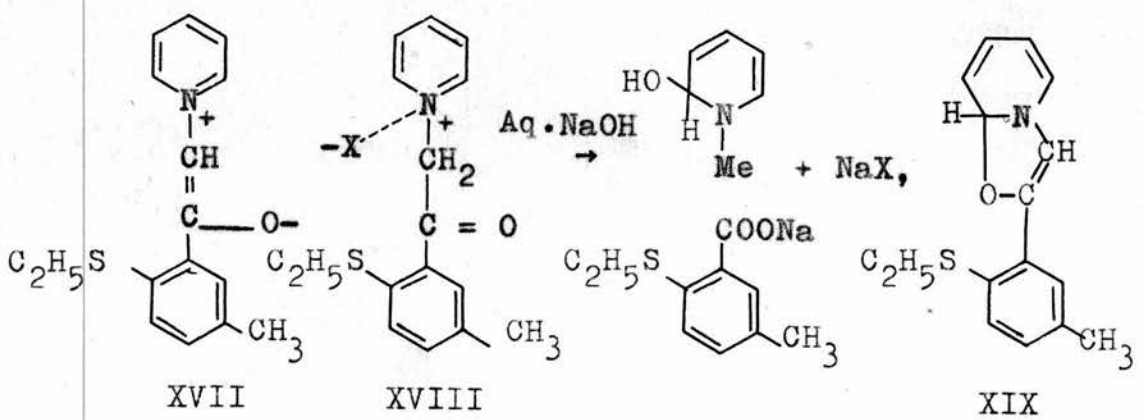


pyridinium bromide with aqueous sodium carbonate, to

give sodium benzoate and N-methyl pyridinium hydroxide XV.

Later workers, Babcock and Fuson (J. Amer. Chem. Soc., 1933, 55, 2946) showed that the pyridinium compound, produced, could be oxidised by alkaline ferricyanide to N-methyl pyridone XVI, presumably through the pseudo base. The formation of a yellow, orange or orange red colour on treatment of such phenacyl pyridinium halides, with alkali, was observed by Bamberger (Ber., 1887, 20, 3338), but he could not account for it. Krohnke (Ber., 1933, 66, 605-608) also got the same colour, but failed to isolate the compound responsible for it.

The first enol betaines, derivatives of N-(hydroxy vinyl) - pyridinium hydroxide anhydro salt XVII were isolated independently, by Krollpfeiffer and Müller, (Ber., 1933, 66, 740) from the mild treatment of the substituted phenacyl pyridinium halides with alkali. If the conditions are too harsh, the well recognised acid fission of the pyridinium salt XVIII, to the acid and the pseudo base, XIX of N-methyl pyridinium hydroxide takes place.

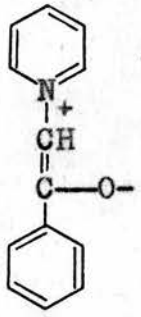


XVII XVIII XIX

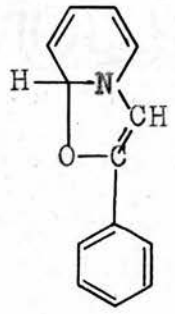
Isolation of these betaines, initiated Krönhke and Krollpfeiffer to a considerable amount of work, on these types of compounds.

The structure of enol-betaines:-

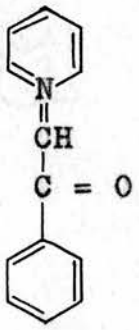
Krönhke (Ber., 1935, 68, 1177-95) isolated the compound from phenacyl pyridinium bromide corresponding to the orange intermediate prepared by Krollpfeiffer in the phenacyl thio ether series, thereby establishing that there were milder conditions, under which, the isolation of the alkali sensitive coloured "intermediates" was possible. The ease of regeneration of the phenacyl pyridinium halide, by treatment of the coloured intermediate with acid, restricted the possible formulations to XX, XXI and XXII.



XX



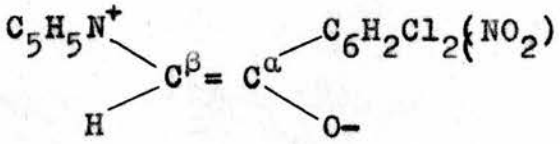
XXI



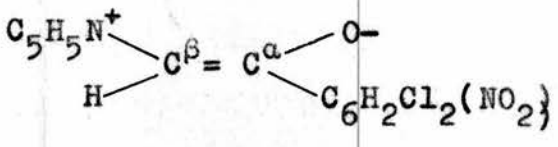
XXII

Structure XXI is incompatible with the high colour of the compound, and XXII, besides conflicting with the modern conception of the nitrogen atom, would involve an evident similarity, to the nitrenes, which does not exist. The enol betaine structure XX is left by elimination; which also agrees with their physical and chemical properties. As evidence

of the presence of the double bond, Krönhke cited the isolation of two forms of N-β (α -hydroxy-3:4 dichloro-2-nitro styryl) - pyridinium hydroxide anhydro salt.



Orange (Labile)



Yellow (Stable)

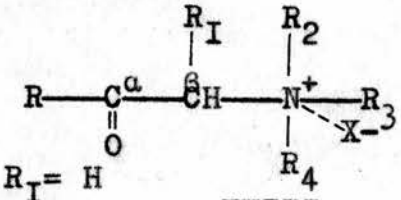
These he formulated as Cis - and trans-isomers.

The requisite molecular specification governing the existence of enol betaines, are the presence in the molecule of:-

(1) An enolisable group.

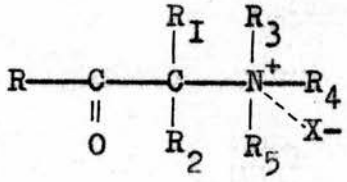
(2) A quarternary nitrogen atom.

Halides of structure XXIII fulfil these conditions, but structure XXIV does not do so, as enolisation is impossible. As halides of structure



(a) R_I= H
(b) R_I= Alkyl
(c) R_I= Acyl Group.

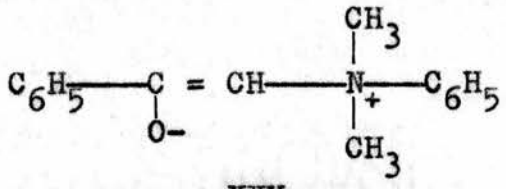
XXIII



XXIV

XXIV do undergo an acid cleavage, (Kroll pfeiffer and Müller, (Ber., 1935, 68, 1169-77) it is apparent that the enol betaines are not essential intermediates in acid cleavage, although the enol betaines do suffer an acid cleavage.

In structure XXIII, R and R_1 may vary widely, and the properties of the resulting betaine are influenced to a considerable extent, by the nature of the substituent. The quarternary nitrogen atom need not be contained in a heterocyclic aromatic compound, since Kröhnke and Heffe (Ber. 1937, 70, 1420) prepared the enol betaine from phenacyl dimethyl-phenyl ammonium chloride XXV. This was colourless, and differed considerably in properties from the corresponding pyridinium compounds.



XXV

Heterocyclic amines are the commonest compounds used in the preparation of betaines, especially, pyridine, quinoline, isoquinoline and the picoline. The derived betaines differ somewhat in depth of colour and in stability.

The preparation and properties of enol betaines is discussed under three heads.

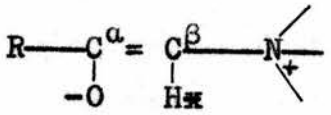
(1) Methine enol betaines. XXIII (a)

(2) ω-alkyl phenacyl betaines. XXIII (b) R=Aryl.

(3) ω-acyl phenacyl betaines. XXIII (c) R=Aryl.

(1) Methine enol betaines:- These are of two types (a) derived from aromatic heterocyclic bases (b) derived from quarternary ammonium nitrogen viz. dimethyl anilinium cation.

Krohnke and Kubler (Ber.,1937, 70, 538) named enol betaines of structure XXVI as the methine enol betaines; because of the reactivity of the methine, ✱, hydrogen atom.



XXVI

(a) Methine enol betaines of the pyridine series are strongly basic substances which are not high melting. They crystallise as yellow or orange hydrates, in contrast to orange or red, anhydrous or less hydrated forms, (In analogy with phenol betaines).

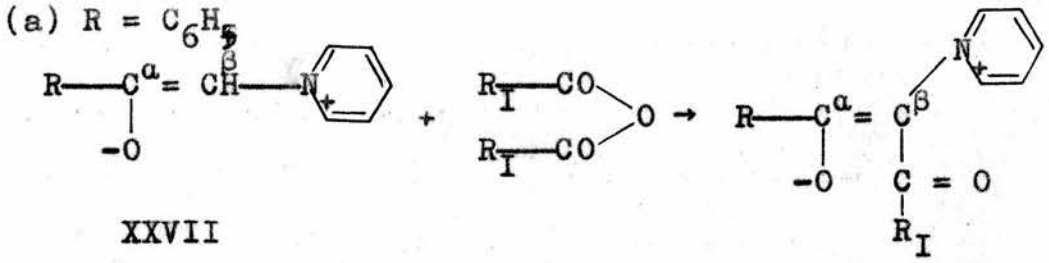
Their most characteristic chemical feature is the reactivity of the methine (β) hydrogen atom, shown by a Zerewitinoff determination and by a series of condensation reactions.

A Zerewitinoff, active hydrogen atom determination confirmed the presence of one active hydrogen atom, per molecule (Krohnke and Kubler,Ber., 1937, 70, 538) of the betaines XXVII.

The hydrogen atom is also readily replaced by acyl groups when the betaines react with acid chlorides or anhydrides. (Krohnke, Ber.,1935, 68, 1177-95. Ber.,1937, 70, 1114) to give ω-acyl pyridinium betaines.

R = aryl

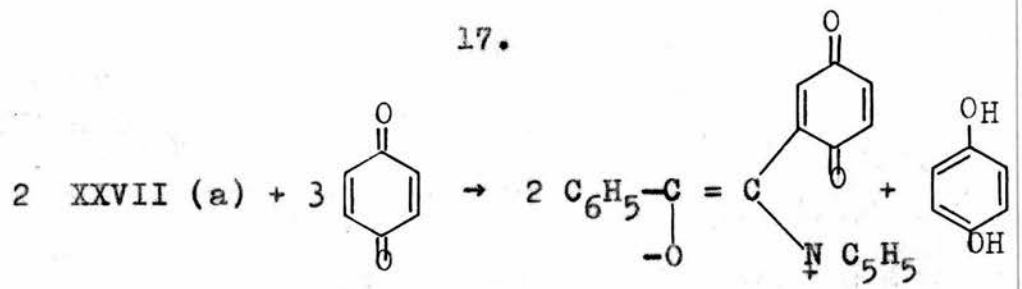
(a) R = C_6H_5



XXVII

The condensation reaction of these compounds are most significant, and are exactly analogous with the reactions of 1:3-diketones and β-diketo esters. [Krönhke (Angewante. Chem., 1953, 65, 605-28), suggests that the reactivity of the methine hydrogen is largely due to pyridinium ring, and less due to the adjacent α-carbonyl group, Because the benzyl pyridinium betaines also give the same condensation reactions as the phenacyl pyridinium betaines.] In the condensation reactions the betaines themselves react, but the phenacyl pyridinium halides may be used instead, together with one molecular proportion of alkali.

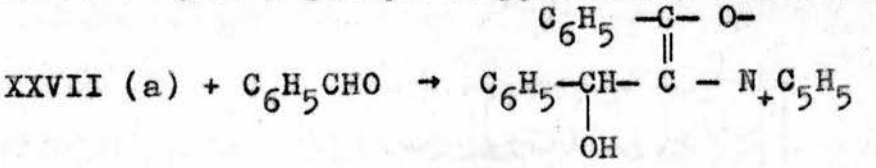
With picryl chloride, or 2:3-dichloro naphthoquinone (Krönhke and Schmeiss, Ber., 1937, 70, 1728-32) XXVII (a) gives an intensely coloured betaine; with elimination of hydrogen chloride and replacement of β-hydrogen atom by a trinitrophenyl or, 2-(3-chloro-1:4-naphtho quinonoid) group respectively. With p-quinone a coloured quinonoid betaine XXVIII was obtained, and the course of reaction was shown to be presumably,

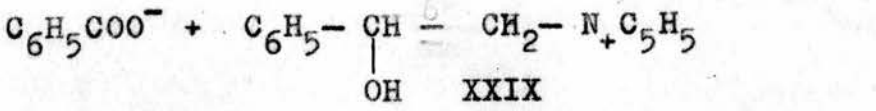


XXVIII

because on carrying out the reaction in an atmosphere of nitrogen, hydro quinone or quin hydrone was obtained simultaneously.

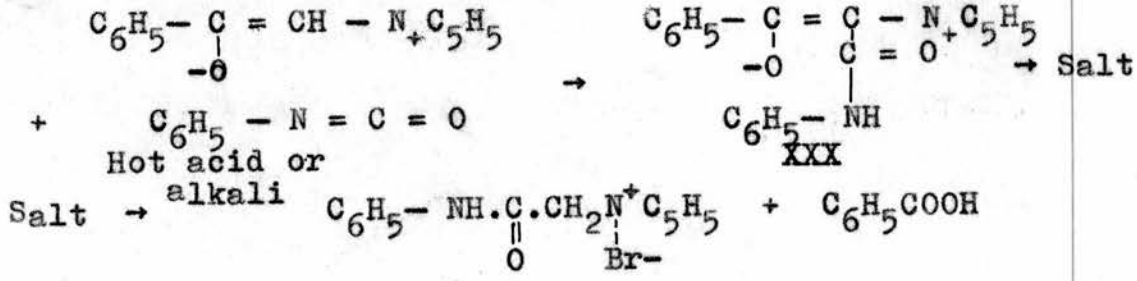
With benzaldehyde (Krohnke, Ber., 1935, 68, 1177; Ber., 1933, 66, 604) the initial condensation product of the aldol type was not isolated, for acid fission occurred to give 1-phenyl-2N-pyridinium ethanol XXIX





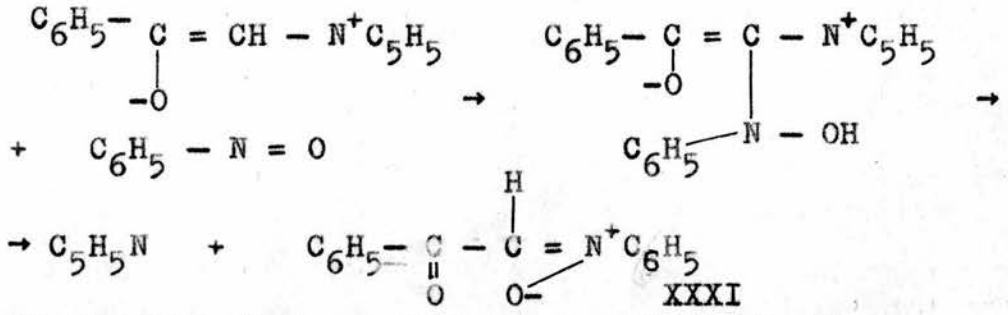
XXIX

With phenyl isocyanate (Krohnke and Kubler, Ber., 1937, 70, 538) the product was the betaine XXX. This gave a stable crystalline hydrobromide, which on treatment with hot acid or with alkali, caused, acid fission, giving benzoic acid and acetanilide-ω-N-pyridinium halide.



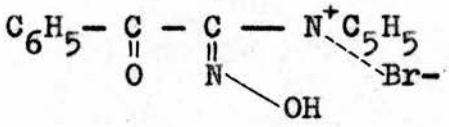
Nitrosobenzene (Krohnke and Borner, Ber., 1936,

69, 2006-16) reacts with methine enol betaines, but the initial products in this case suffered loss of pyridine and a nitrone XXXI was isolated.



The nitrone XXXI, when treated with acid gives, phenylhydroxyl amine $C_6H_5.NH.OH$ and phenyl glyoxal $C_6H_5.CO.CHO$.

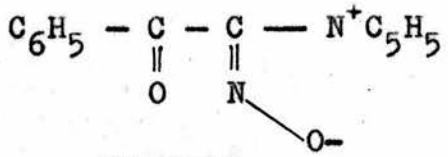
Kröhnke and Kübler (Ber.,1937, 70, 1117) found that phenacyl pyridinium bromide reacted with ethyl nitrite in an alcoholic alkaline solution, giving a crystalline but an unstable betaine. This gave a stable bromide. They therefore formulated it as XXXII.



XXXII

Its treatment with aqueous sodium carbonate gave yellow needles, presumably the extremely unstable isonitroso-betaine XXXIII, which if put on glass or clay, spontaneously decomposed with deflagaration to give benzoic acid, pyridine and hydrogen cyanide. On rubbing in alcohol, it changed into red needles, M.P. 42°c. But, unfortunately the analyses of these

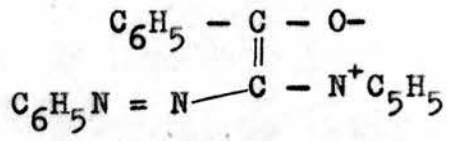
unstable substances was impossible, though from their methods of preparation, they



XXXIII

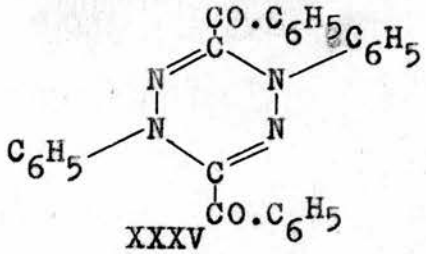
appear to be betaines. Krönhke and Kübler discussed the interesting possibility of cis- and trans-isomerism in this analogue of benzil. monoxime.

Krollpfeiffer and Braun (Ber., 1937, 70, 89-95) showed that phenacyl pyridinium salts, gave with benzene diazoniumchloride and sodium acetate, a red betaine XXXIV. This on heating lost pyridine

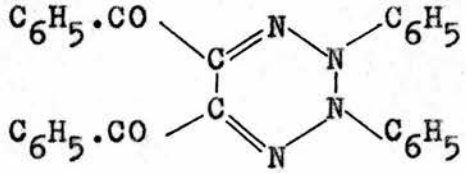


XXXIV

and the remainder of the molecule gave a dimeric product of a cyclic tetrazine type, which was either 1:4-diphenyl-3:6-dibenzoyl-1:2:4:5 tetrazine, XXXV, or 2:3-diphenyl-5:6-dibenzoyl-1:2:3:4 tetrazine;



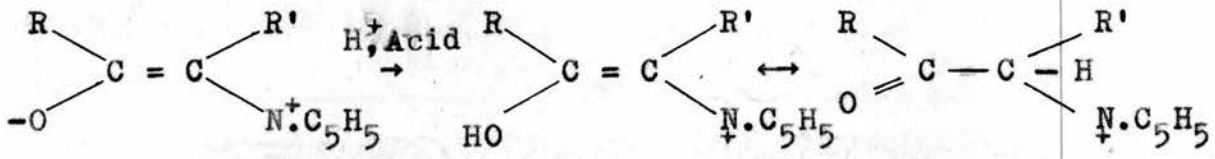
XXXV



XXXVI

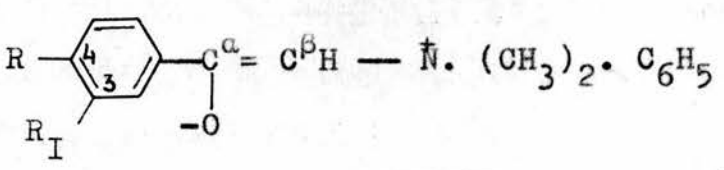
The methine enol betaines of the pyridinium series, are a group of reactive substances by virtue

of a reactive hydrogen atom. These enol betaines are very basic substances. Even suspending them in water and passing carbondioxide through the suspension, renders the solution colourless. This basicity is associated with the enol group, and occurs not only in the methine enol betaines but also in ω-alkyl-phenacyl-pyridinium enol betaines.



R' = H, alkyl.

(b) Quarternary ammonium-methine enol betaines:- Only a few methine enol betaines derived from phenacyl dimethyl anilinium halides are known. (Krönhke and Heffe., Ber., 1937, 70, 1720). They are N- β -(α-hydroxy-4-bromostyryl)-dimethyl anilinium anhydro salt, XXXVII (a) and the related, 3:4-dichloro, XXXVII (b), and 3-nitrostyryl, XXXVII (c), compounds.



(a) R = Br, R_I = H
(b) R = R_I = Cl
(c) R = H, R_I = NO_2

XXXVII

XXXVII (a) and (b) are both colourless, but XXXVII (c) was red. The reason for this is shown by Krönhke and Heffe, to be due to a molecular complex being formed, involving nitro and the anilinium group. Because, when XXXVII (a) or (b) were dissolved in nitrobenzene, an orange solution was obtained

Apart from this difference in colour, all the three showed similar properties.

The colourless nature of these quarternary ammonium betaines, in contrast to highly coloured betaines of the pyridine series, was discussed by W.H. Stafford (J.,1952, 580). He attributed this feature, to the fact that the anilinium cation, unlike the pyridinium cation, is not involved in resonance with the rest of the structure of the betaine molecule, due to absence of conjugation. He stated that such resonance as furnished by the pyridinium cation, is essential for colour. This phenomenon is also missed in the amphoteric betaines which are colourless.

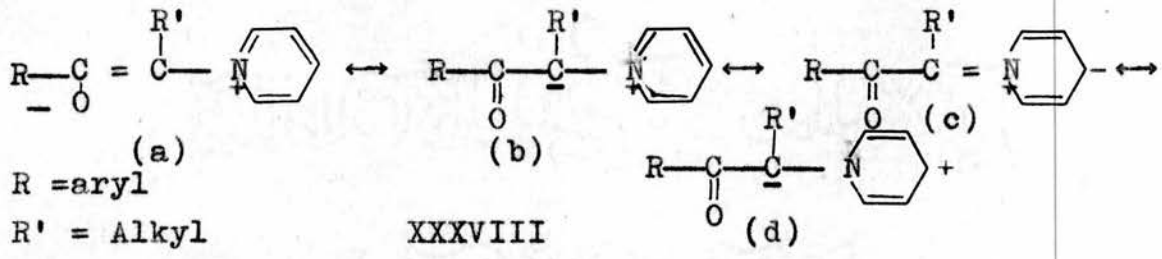
The methine hydrogen atom in these anilinium betaines is unreactive. Thus no coloured compounds comparable to those in the pyridine series, were obtained either with picryl chloride or chloranil. Unlike the pyridinium enol betaines, which reacted with benzoyl chloride and benzoic anhydride to give C-benzoyl compounds, these reacted only to give O-benzoyl compounds. There is no reaction with isocyanates, aldehydes or diazonium compounds. It does however react with nitrosobenzene, on warming, to give the nitrone XXXI by the loss of dimethylaniline.

Replacement of pyridine with dimethyl aniline in methine enol betaines, causes two fundamental alterations in properties, the first is in colour and second

is in the reactivity of the β hydrogen atom.

(2) <u>ω-alkyl phenacyl pyridinium anhydro salts</u>:-

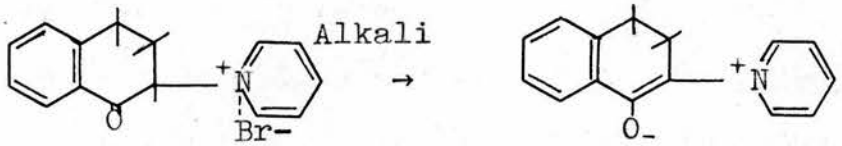
The enol betaines derived from w-alkyl phenacyl pyridinium salts differ from the corresponding methine enol betaines only in their inability to suffer condensation reactions - described before. They resemble them, in all other properties, method of preparation, colour, basicity and tendency to form hydrates. Their general formula could be put as:



R =aryl
R' = Alkyl

XXXVIII

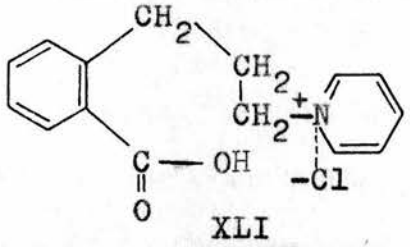
and the various contributing forms justify their colour and stability. A member of this group has been examined with thoroughness by Krollpfeiffer and Müller (Ber., 1935, <u>68</u>, 1169) the 1-tetralone-2N-pyridinium enol betaine XXXIX, which was derived from 1-tetralone-2-N-pyridinium bromide XL in the usual way.



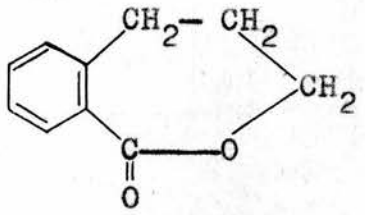
XL XXXIX

This compound was isolated, apparently in a hydrated form and, as is so often experienced with hydrates, a satisfactory analysis was difficult to obtain. Alkaline treatment followed by acidification,

was shown to yield (by normal acid cleavage) ω-(O-carboxyphenyl)-n-propyl-N-pyridinium chloride. XLI. This on distillation gave the



XLI



XLII

lactone of O-carboxyhydrocinnamyl alcohol XLII.

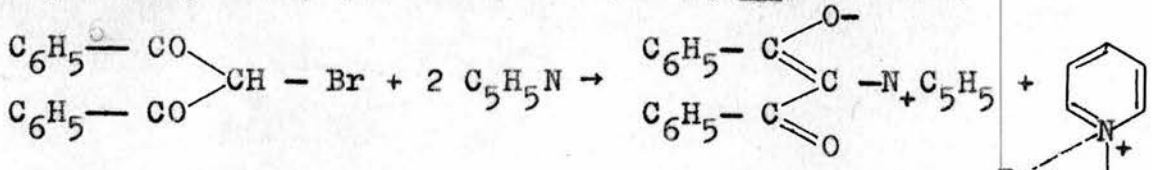
ω-acyl phenacyl pyridinium enol betaines:- The general representation of such a betaine is, XXXVIII (a) with R′ = acyl group.

The C-benzoyl pyridinium enol betaine XLIII, has been prepared by three methods:-

(1) By the reaction of phenacyl pyridinium enol betaine with benzoic anhydride.

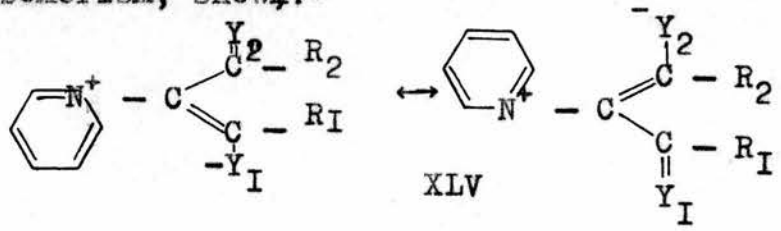
(2) By reaction of phenacyl pyridinium enol betaine with benzoyl chloride.

(3) By the action of pyridine on w-bromo-w-benzoyl acetophenone, XLIV, (Krohnke, Ber., 1935, 68, 1177-95)



XLIV XLIII

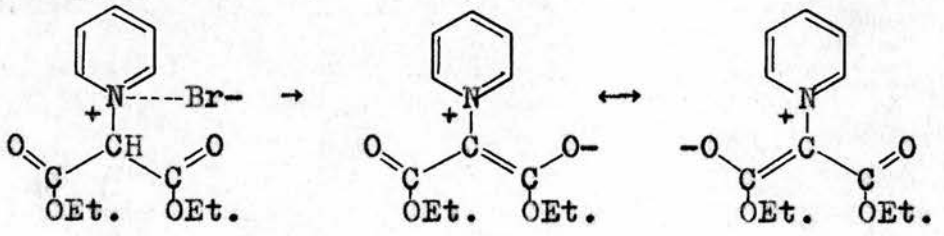
Krohnke swiftly realised that compounds similar to XLIII, i.e. of general formula, XLV, are capable of the mesomerism, shown:-



XLV

This was supported by Kröhnke's discovery, that any attempt to synthesise compounds, possessing the structures of the two canonical forms gave only one product, e.g., the reaction of p-bromo benzoic anhydride with phenacyl pyridinium enol betaine gave the same product, as the reaction of benzoic-anhydride with p-bromo phenacyl enol betaine.

Kröhnke prepared several compounds of this type, and one of the most novel was that derived from malonic ester -2N-pyridinium bromide, XLVI , (Ber., 1937, 70, 543). This is a stable, high melting, yellow crystalline solid.



XLVI (Betaine)

Compounds of this general type are, as would be expected, very different from the enol betaines previously described.

(1) They are less reactive and do not give the same colour reactions or the condensation reactions.

(2) They are stable.

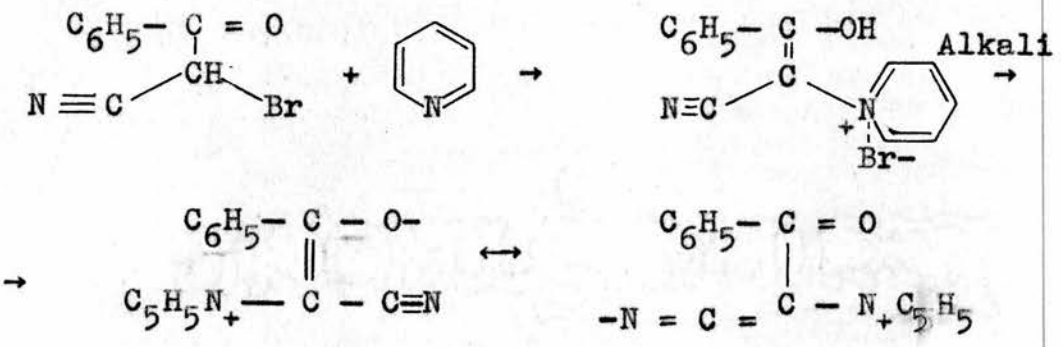
(3) They are high melting.

(4) They have higher solubilities in polar

solvents.

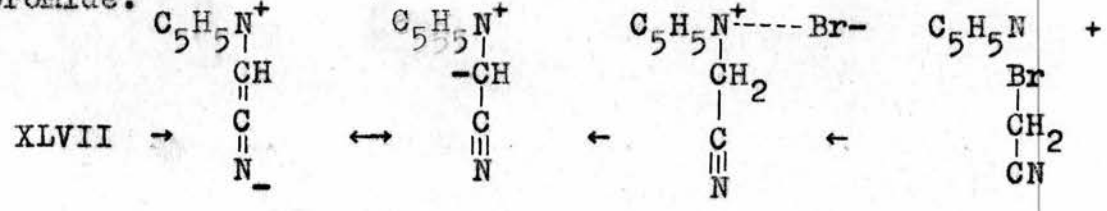
(5) They are neutral.

Several variations of the above mentioned type of compounds are known, for example, Kröhnke (Ber., 1939, 72, 83-9) prepared w-cyanophenacyl pyridinium enol betaine, XLVII in the usual way.



XLVII

This betaine suffered an acid cleavage to yield the betaine XLVIII, which was also prepared by the action of alkali on w-cyano-N-methyl-pyridinium bromide.



XLVIII

A less clearly defined case was that of the w-nitrosophenyl pyridinium enol betaine XLIX, obtained by the action of alkyl nitrites on phenacyl pyridinium enol betaines, in presence of alkali (Kröhnke, Ber., 1937, 70, 1117-20)

(a) ↔ (b)

XLIX

The compound was extremely unstable and Krohnke claimed the isolation of the isomers, postulating that these were stereoisomers XLIX (a) and (c).

(a) (c)

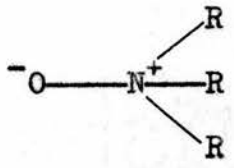
XLIX

If it is true, then stereoisomerism involving significantly XLIX (b), is impossible, as this would tend to alter the character of C=N group responsible for any stereoisomerism.

The Ylides:- Under the head of C-betaines are classified a series of compounds, known as "Ylides". This nomenclature of the C-betaines, was, put forward by G. Wittig (Wittig, Annalen, 1945, 557, 201), and is intended to suggest the coexistence of covalent (yl-) and ionic (-ide), characteristics, in the compound.

A compound of this type, the red triphenyl-methyl-tetra alkyl ammonium betaine was first reported by W. Schlenk and A. Holz (Ber., 1916, 49, 603; Ber., 1917, 50, 274). Later Ingold and Jessop

(J.,1929, 2357) while examining the degradation of quarternary ammonium hydroxides, observed the formation of coloured intermediates, and they ascribed the colour to the dipolar form of an anhydro salt. They referred to such compounds as "ylidides" to express the partial polar character (J.,1930, 713). From the comparison of the amine oxide I, and that of the corresponding sulphur compounds, the sulphoxides II, they concluded that the dialkyl sulphonium hydroxide anhydro salts would be more stable. This conclusion was supported by their



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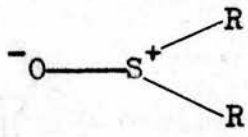
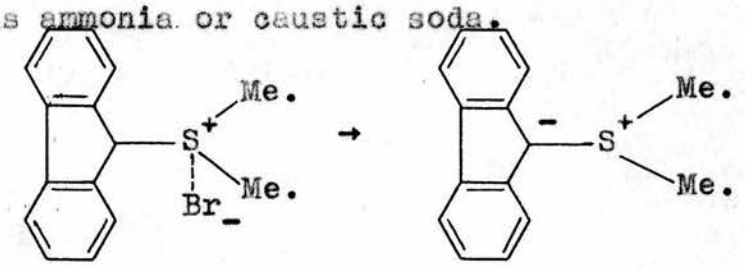


II

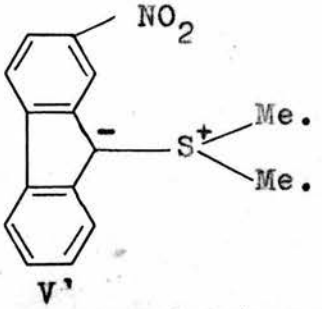
isolation of the sulphonium anhydro salt IV, in the crystalline form. This decomposed after some hours with the evolution of dimethyl sulphide. Compound IV, is dimethyl sulphonium 9-fluorenylide (an ylide) obtained from the salt III on treatment with aqueous ammonia or caustic soda.



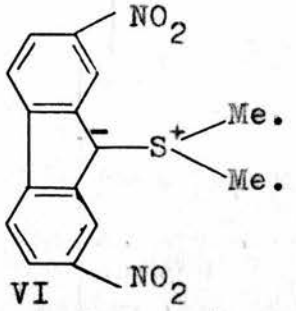
III IV

Hughes and Kuriyan (J.,1935, 1609) extended this work by isolating 2-nitro, V, and the 2:7-dinitro VI, derivatives of IV. The first 'V' was a purple

crystalline compound, obtained from acteone solution, and was stable for several days, and the second, VI, had



V'

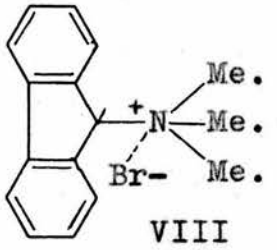


VI

the appearance of potassium permanganate, and was indefinitely stable. This could even be titrated in polar solvents against acids. The crystals were not soluble in water alone.

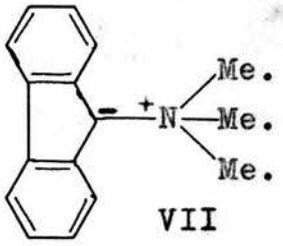
Krollpfeiffer and Schneider (Annalen, 1937, 530, 38) while considering enol betaine structures, recognised that the colour of "Ylidides" was due to dipolar grouping. They mention the deep blue colour obtained by the action of alkali on fluorenyl 9-pyridinium salts.

Wittig (Annalen, 1944, 555, 133) succeeded in isolating the orange red 9-trimethyl ammonium fluorenylide VII, betaine under nitrogen. The ylide decomposed in air to give trimethyl amine, and dissolved rapidly in water to give the hydroxide. The ylide was obtained readily, on treatment of 9-trimethyl ammonium - fluorenyl bromide, VIII, with phenyl lithium in ether solution.



VIII

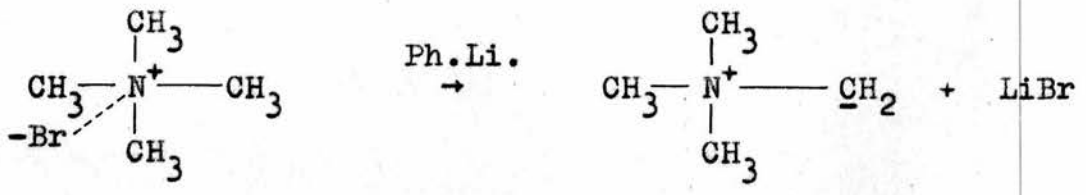
→ Ph. Li.



VII

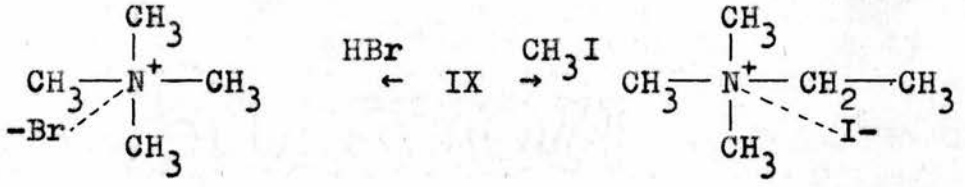
+ LiBr

In an anologous manner, Wittig was able to show the formation of trimethyl ammonium methylide IX, obtained by treatment of tetramethyl ammonium bromide X with phenyl lithium (Wittig, Annalen,1945, 557, 193).

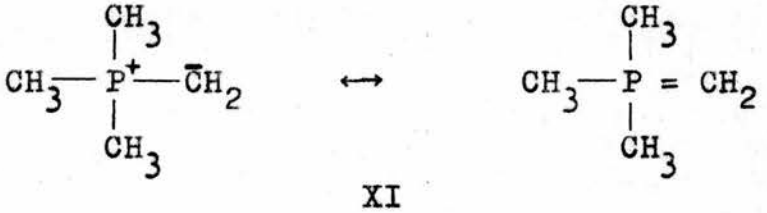


X IX

The ylide IX is extremely unstable. It readily adds an alkyl halide e.g. methyl iodide, or acids, to give stable salts.



This method was extended by Wittig (Annalen, 1949, 562, 187) to the preparation of phosphonium methylide XI, which he obtained from tetra methyl phosphonium bromide on treatment with methyl lithium. The ylide readily adds methyl iodide to give an addition product.

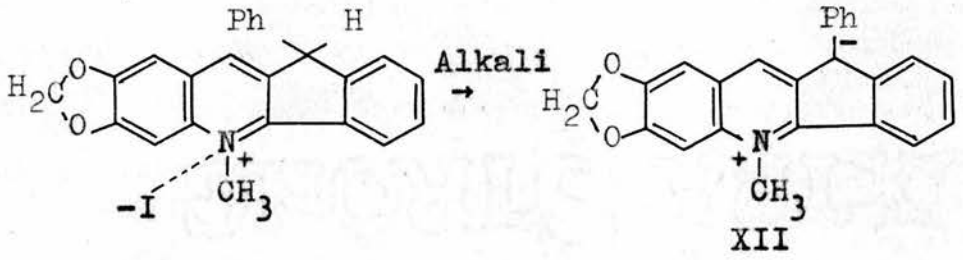


XI

The work was later on extended to trimethyl phosphonium fluorenylides, which were more stable

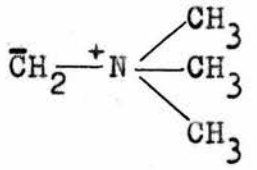
than the corresponding ammonium fluorenylides.

An interesting compound of this category was obtained by Armit and Robinson (J.,1925, 1607), who reported the anhydronium base, N-methyl-7:8 methylene-dioxy-11-phenylindenoquinolinium hydroxide anhydro salt XII, as a green coloured crystalline solid. This compound was susceptible to oxidation as the rest of the ylides.

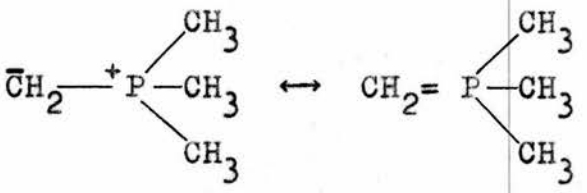


The preparation of ylides involves the formation of an anhydro "ONIUM" hydroxide. This is achieved by the use of quarternary salts, e.g. ammonium, pyridinium, quinolinium, isoquinolinium etc., types of structures, which provide the cationic centre, whilst an anionic centre is developed on a carbon atom, in the structure, by the loss of a proton.

The stability of an ylide depends upon the energy of the resulting dipolar molecule. Where, there is resonance, the stability is increased, and it will also be increased by the presence of deactivating substituents. Some of the ylides and their stability are given below.



(Transient)



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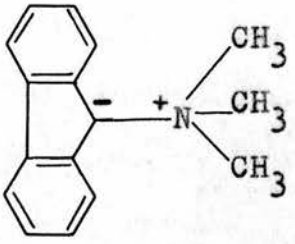
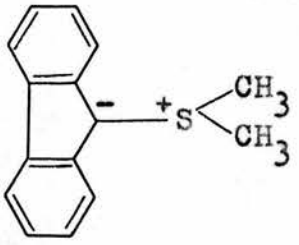


(Stable only under nitrogen)



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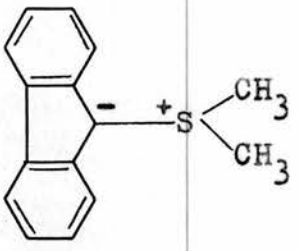

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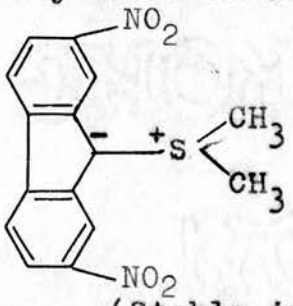
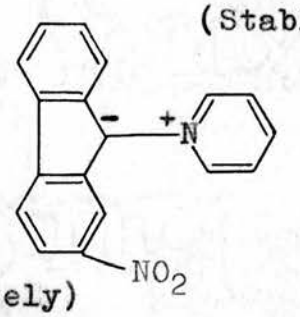




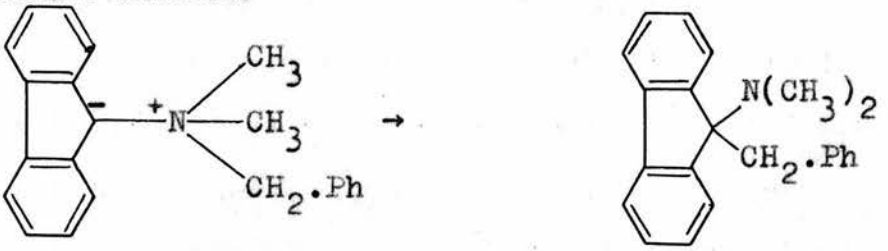
(Stable indefinitely)

Ylides are chemically unstable, and in many cases they have a fleeting existence. This has been attributed to the great susceptibility of the carbon anion to the atmospheric oxygen, which causes oxidation. Some ylides are also photo sensitive. (See later).

Ylides have been shown to undergo an internal rearrangement (Stevens, J., 1928, 3193; J., 1930, 2107-2119; J., 1932, 55, 1926) involving the rearrangement of a quarternary ammonium salt to a tertiary amine, of the type given below.

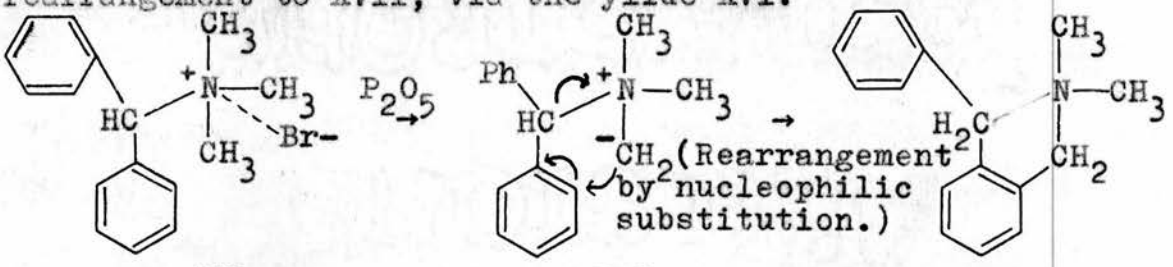
The ylide XIII quickly rearranges into the tertiary amine XIV, as soon as it is generated, in

an alkaline medium.



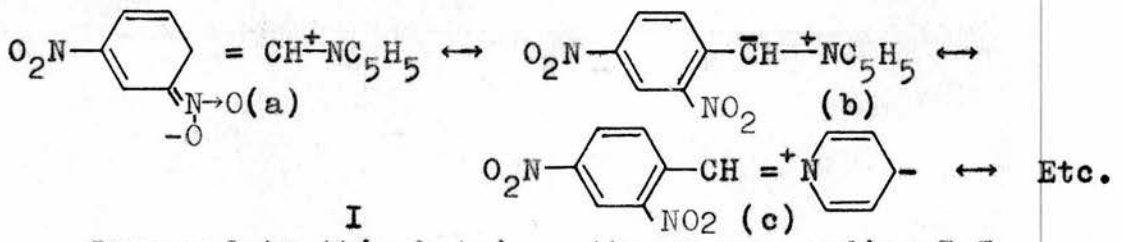
XIII XIV

Another example of an induced rearrangement, is that of Sommelet's (Compt. Rend., 1937, 205, 56) which is explained on the basis of ylide formation. He used benzhydril-trimethyl ammonium hydroxide XV and treated it with phosphorus pentoxide, to induce the rearrangement to XVII, via the ylide XVI.



XV XVI XVII

The Aci-nitro betaines:- A typical betaine of this type, was obtained by Krohnke (Ber., 1939, 72, 440) as a crystalline blue black compound derived from 2:4-dinitrobenzyl pyridinium bromide; M.P. 124-26° c. This was formulated as a resonance hybrid of various contributing forms, e.g. I (a), (b) and (c).



I

Compared to this betaine, the corresponding 3:5-dinitrobenzyl pyridinium betaine (Krohnke, Ber., 1937,

70, 1118) is less deeply coloured. Barnett and Co-workers (J.,1929, 505; J.,1926, 1035) were the first to note the existence of such betaines. All the acinitro betaines give violet red coloured compounds with picryl chloride, and are extremely reactive substances, readily undergoing condensation reactions; e.g., with p-nitrosodimethyl aniline, nitrones were obtained, which hydrolysed with acid to the nitrobenzaldehydes. They are therefore analogous to the corresponding methine enol betaines. Their deep colour and reactivity is due to the contribution of $-\bar{C}<$ ionic structure to the resonance hybrid.

The Enimine Betaines:- The simplest enimine betaine is the yellow anhydro salt, II, Krönhke (Ber., 1939, 72, 85) derived from N-cyano methyl pyridinium halides by reaction with alkali.

$$C_5H_5N^+ - \bar{C}H - CN \longleftrightarrow C_5H_5N^+ - CH = C = \bar{N}$$

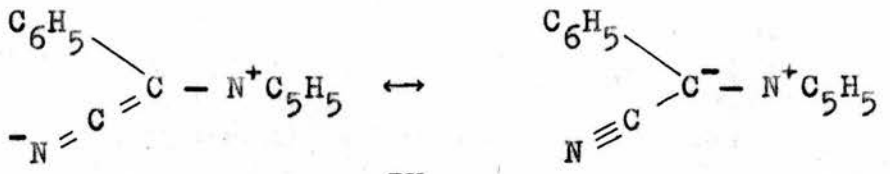
II

$$C_6H_5 - C = O \longleftrightarrow C_6H_5 - C - O^-$$
$$\bar{N} = C = C - N^+C_5H_5 \qquad\qquad N\equiv C - C - N^+C_5H_5$$
(a) III (b)

This is a typical $-\bar{C}<$ ionic type betaine and is very reactive, condensing readily with benzoyl chloride to give the anhydro salt III (a) enimine (b) enolate.

A deep violet coloured anhydro salt, IV, of this series was formed by the reaction of ω-cyano benzyl pyridinium bromide with potassium carbonate

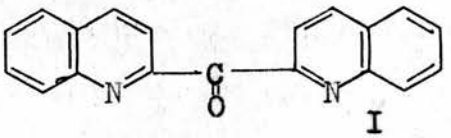
Krohnke (Ber.,1939, 72, 85).



IV

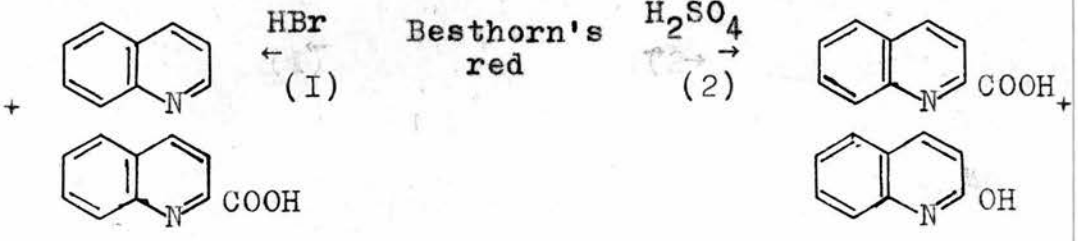
In the enimine betaines the anionic centre is afforded by a nitrogen atom, which is in resonance with the $-\bar{C}$ ionic form. The latter form is responsible for their colour and reactivity, comparable to methine enol betaines.

Besthorn's Red:- Besthorn and Ibele isolated from the decarboxylation of quinaldinic acid in acetic anhydride, a light sensitive, red substance; formula $C_{19}H_{12}ON_2$, which crystallised as red pleochroic needles. It was weakly basic, and, although it gave no ketonic reactions, it was given the preliminary formulation of 2:2'-diquinolyl ketone I, because of two degradations:



I

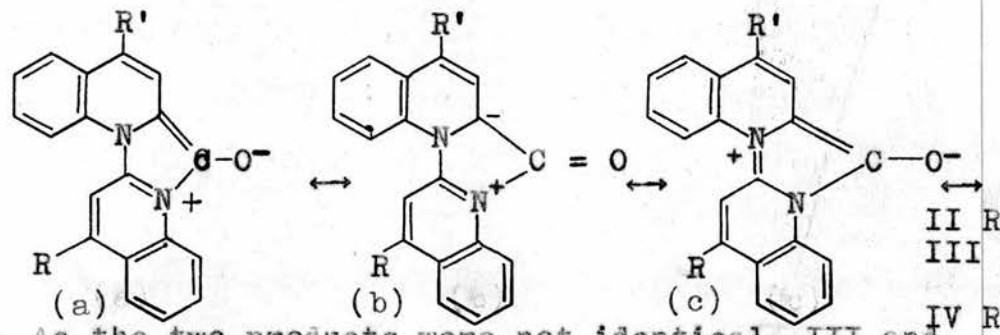
(1) With hydrogen bromide, to quinoline and quinaldic acid and (2) with sulphuric acid to carbostyril and quinaldic acid.



This symmetrical structure was disproved.

(Besthorn,Ber.,1913, 36, 2762) by the synthesis of two mono-phenyl substituted derivatives by reciprocal methods.

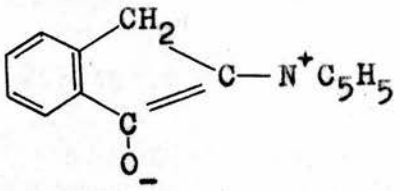
(1) From the reaction of quinaldic acid chloride with 4-phenyl quinoline, and (2) from the reaction of 4-phenyl quinaldic acid chloride with quinoline.



As the two products were not identical, III and IV, the symmetrical structure was replaced by a Pentacyclic structure, which, when modified by Krollpfeiffer and Schneider (Annalen, 1937, 530, 34) to confirm with modern concepts of covalency of nitrogen, became II. An alternative diradical structure was shown to be irreconcilable with the magnetic susceptibility of the substance. (Krollpfeiffer and Schneider, Annalen, 1937, 530, 34).

All the compounds related to Besthorn's red are photo sensitive. The absorption spectra, however has been determined, for the parent compound in alcohol (λ max = 490 mμ) and in benzene (λ max = 570 and 520 mμ). This pronounced shift on changing the solvent was ascribed to the change in the dielectric constant of the medium which was assumed

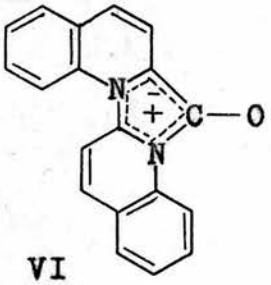
to affect the relative contributions of the various dipolar canonical forms. Light sensitivity and similar displacement of absorption maxima (λ max in alcohol 440 $m\mu$, λmax in water 420 $m\mu$) have been shown for another anhydro salt - V (Stafford; J., 1952, 580)



V

This as will be shown later has been found to be a common feature of the anhydro salts which goes to suggest the coloured enol betaine structure II (b) and (c) for Besthorn's Red.

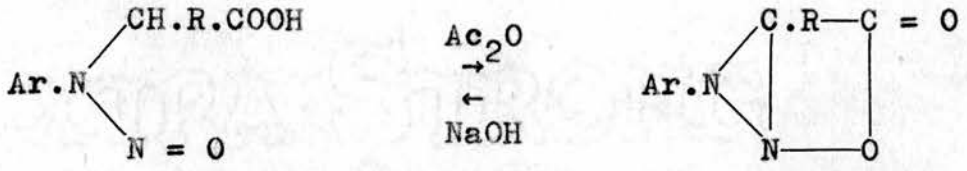
Hammick and Roe (Chem. and Industry, Aug. 22nd., 1953) formulate Besthorn's Red as a mesoionic structure VI, which means a resonance hybrid of a number of covalent formulae, and



VI

that there is no well developed positive or negative charge on any one atom of the hetero-five membered ring. This however does not explain the origin of the colour, which could be best attributed to the betainoid forms II (b) and (c).

Sydnones:- The work of J.C. Earl and his collaborators has shown that the N-nitroso-N-arylglycines (I, R=H) readily lose a molecule of water when treated with acetic anhydride at room temperature, to give unimolecular anhydro-compounds (Earl and Mackney, J., 1935, 899; Eade and Earl, J. 1946, 591). The reaction also occurred in the case of N-nitroso-α-anilino-propionic acid (I; R=Me; Ar=Ph), but not with N-nitroso-α-anilinoiso butyric acid, $Ph.N(NO).C\,Me_2.\,CO_2H$. As these anhydro-compounds had been prepared in the University of Sydney, they were termed "Sydnones", the anhydro-derivatives of N-nitroso-N-phenylglycine being referred to as N-phenyl sydnone.



I II

The sydnones were shown to be neutral, highly crystalline, stable compounds, fairly soluble (except p-nitrophenyl sydnone) in most organic solvents including benzene. They are generally low melting (N-p-tolyl sydnone, M.P. 142°-44°c; N-benzyl sydnone, M.P. 69.5°c.) and are colourless. They do not absorb light above 350 mμ (C-phenyl-N-phenyl sydnone, λmax = 335 mμ; N-phenyl-sydnone, λ max = 310; N-benzyl sydnone, λ max = 290 mμ). Hill and Sutton have measured the dipole moments of several sydnones,

and the values are high, usually 6-7. D. (Hill and Sutton, J.,1949, 746).

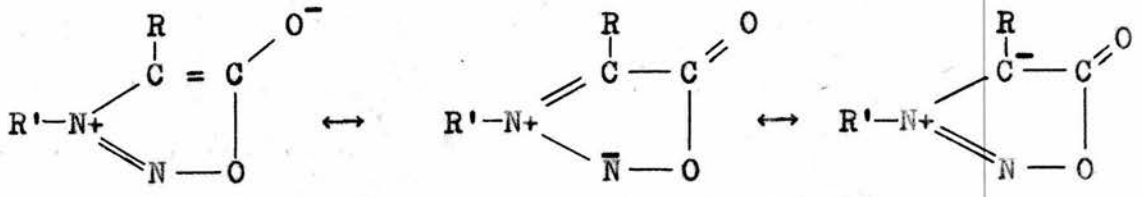
When hydrolysed with hot, dilute alkali they regenerated the N-nitroso-N-arylglycines, but hydrolysis with hot, concentrated hydrochloric acid gave one molecule each of an aryl-hydrazine and formic acid, carbon dioxide also being evolved. In the case of the sydnone derived

$$\text{II} \xrightarrow[\text{Con. HCl}]{\text{Hot}} \text{Ar.NH.NH}_2 + \text{RCOOH} + \text{CO}_2$$

from N-nitroso-α-anilinopropionic acid, acetic acid was produced in place of formic acid.

The structure II, the "lactone of 2-hydroxy-1-phenyldiaziridine-3-carboxylic acid" was tentatively suggested for these compounds, it contains fused, 3 and 4 membered rings, the latter being of the β-lactone type. This formulation, however was found incompatible and inconsistent with the properties of these compounds by Baker (Baker and Ollis, Nature, 1946, 158, 703), and later on by its proposers (Earl, Nature,1946, 158, 909), based on several pieces of evidence.

Hill and Sutton, inferred from their dipole-moment measurement of sydnones that the significant contributing structures were III (a), (b) and (c).



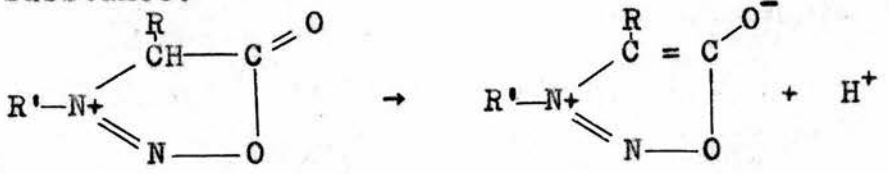
(a) (b) (c)

R = H, alkyl or aryl.
R'= Alkyl or aryl. III

From the lack of colour of the sydnones, a large contribution of the —C ionic type would be improbable - a fact confirmed by Hill and Sutton. This lack of colour must be due to the fact that, structure III (a) is the principal contributant (Cf. the enol betaines of the dimethyl anilinium series), but the [illegible] basicity in sydnones is low.

(Baker, Ollis and Poole, J.,1949, 307) proposed a modified hybrid structure of aromatic type, consisting of a number of contributing forms which include the types III (a), (b) and (c) etc. The term "Mesoionic" was suggested for compounds of this type.

The mechanism of formation of sydnones as postulated by Baker, Ollis and Poole, is closely allied to that of enol betaine formation. The last stage involves the loss of a proton from a cationic type of substance.



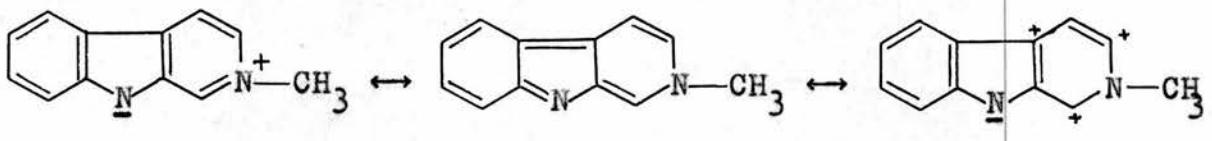
Anhydro salts derived from 3-amino pyridine:-

A number of coloured alkaloids containing as

their essential nucleus, a 3-amino pyridine residue are known and have been formulated as resonance hybrids involving major contributions of anhydro salt structure. One of the simplest is the violet alkaloid cryptolepine (Gallert, Raymond, Hammet and Schlittler, Hel. Chem. Acta., 1951, 34, 642) which is usually obtained as a crystalline hydrate. Its structure is I (a) with possibly some contribution of (b), the ortho-quinonoid form.

(a) I (b)

Schwarz and Schlittler (Hel. Chem. Acta., 1951, 34, 629) have studied various alkaloids of the serpentine group and have shown that their colour, absorption spectra and chemical properties closely ally them to N-methyl-nor-harman II, which they represent as the resonance hybrid of the structures (a), (b) and (c), in which anhydro salt forms are very important.



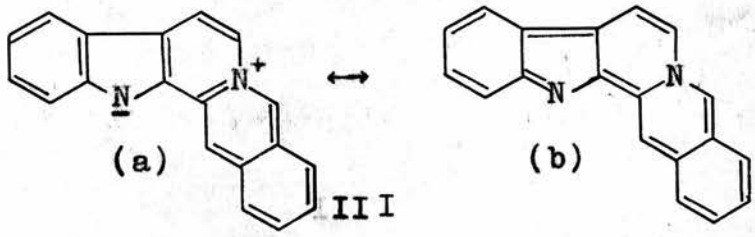
(a) (b) (c)

II

II is a deep yellow substance and its absorption is identical in shape with the serpentine alkaloids.

Witkop and Woodward have formulated (J. Amer.

Chem. Soc., 1949, 71, 379) the structure of sempervirine as a resonance hybrid in involving as an important contributant the anhydro salt form III (a).



From chloroform sempervirine crystallises as yellow needles (M.P. 228°C) and from aqueous alcohol as dark yellow plates (M.P. 258°C). On drying however these two forms gave comparable analyses.

Related compounds, derived from aza-indole, indole and the carbolines will be discussed in a later section.

SECTION (A)

SECTION A.

The $\bar{O}$-betaines:- Absorption spectra of the phenol and enol betaines have been studied, in the visible and ultra violet region with a view to correlate the results with their salt like structure. Although much work has been done on these compounds, yet very little is known about their physical properties like the dipole moments, absorption spectra etc., which would be of great help in explaining their polar character.

The instrument employed for the measurement of spectra in the ultra violet and visible regions was the standard Unicam S.P. 500 Quartz spectrometer. All the solvents employed were specially purified for the spectroscopic measurements, according to the prescribed methods.

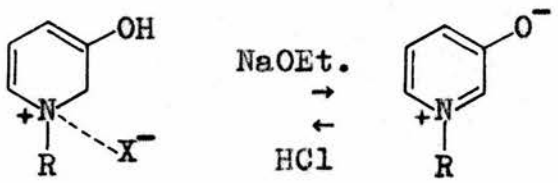
Simplest betaines of this category, with one hydroxyl group (phenolic or enolic) to provide an anionic centre, and a quarternised nitrogen as cation have been chosen. The general procedure adopted is as follows:-

For phenol betaines, hydroxy substituted derivatives of pyridine and quinoline were used as the starting material. These were quarternised by refluxing them with methyl iodide, usually using pure acetone as the solvent. The quarternisation went readily in most cases, with excellent yields, and the products analysed

correctly. The quarternary salt was then treated with aqueous alkali e.g. potassium carbonate or sodium hydroxide of required strength to generate the betaine, which was extracted into chloroform. From a concentrated solution of the betaine in chloroform, the betaine was crystallised by addition of petrol. In some cases where the betaines were elusive, their spectra were taken by liberating them in alkaline ethanol. The phenol betaines as mentioned before were highly hygyroscopic, and their readiness to form hydrates made their analysis difficult.

The phenol betaines which have been studied are given below, their detailed preparation is shown in the experimental section.

N-methyl 3-hydroxy pyridinium hydroxide anhydro salt I:- This was made by quarternising 3-hydroxy pyridine with methyl iodide, and then treating the methiodide with alkali (2N-potassium carbonate). The betaine I gave a colourless solution in chloroform, from which it gave colourless crystals with petrol, which failed to analyse due to its instability, consequently its spectrum was studied by generating it from its methiodide in alkaline ethanol. The betaine II



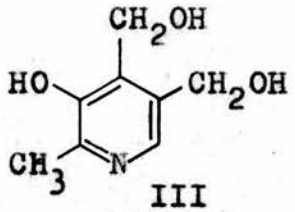
I R = CH_3

II R = -p $(NO_2).C_6H_4.CH_2^-$

obtained from the p-nitro benzyl bromide derivative of 3-hydroxy pyridine however, analysed correctly for a mono hydrate.

Absence of colour in the betaines is noticable which leads to the suggestion, that for colour, the anionic centre of the anhydro salt should be in a separate sphere from the pyridinium ring, the cation. Similar phenol betaines, which have the anion separated from the pyridinium cation, through various ways of conjugation, are highly coloured, as will be shown later.

Stiller, Kereszstesy and Stevens (J. Amer. Chem. Soc., 1939, 61, 1239) in the course of work on vitamin B_6, III, have reported the absorption



III

spectra of 3-hydroxy pyridine in acid (λmax 282.5mμ log ε 3.77) and in alkaline media (λmax 298, log ε 3.63) and (λ max 234 log ε 3.94). Their results provide an interesting comparison with the spectra of 3-hydroxy pyridine in neutral solution, and the, spectra of the derivatives discussed above, shown in table I.

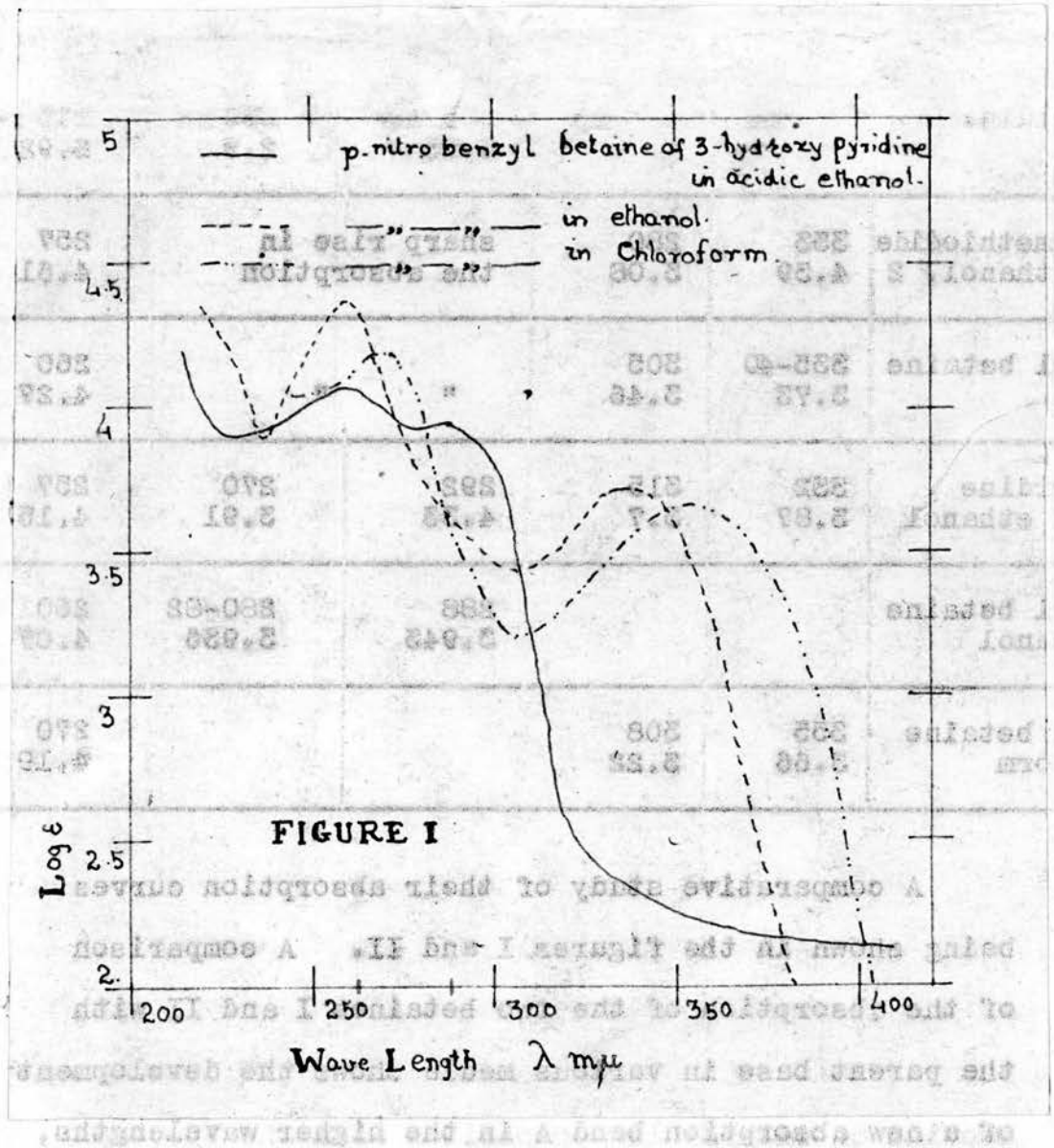

p-nitro benzyl betaine of 3-hydroxy pyridine
in acidic ethanol.
in ethanol.
in Chloroform.
5
4.5
4
3.5
3
2.5
2.
Log ε
200
250
300
350
400
Wave Length λ mμ

FIGURE I

Table I.

	A		B			
Compound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max log ε	λ min. log ε
ydroxy pyridine ethanol	mμ	mμ	280 mμ 3.55	250 mμ 2.9	245 mμ 2.92	240 mμ 2.89
ydroxy py-methiodide alkaline ethanol. 2	333 4.39	280 3.08	sharp rise in the absorption		257 4.61	238 4.21
itro benzyl betaine in ethanol	335-40 3.73	305 3.46	" "		260 4.27	237 3.9
ydroxy pyridine hiodide in ethanol	332 3.87	315 3.7	292 4.33	270 3.91	257 4.15	245 3.96
itro benzyl betaine acidic ethanol			288 3.943	280-82 3.936	260 4.07	238 3.93
tro benzyl betaine in chloroform	355 3.66	308 3.22			270 4.19	

A comparative study of their absorption curves are shown in the figures I and II. A comparison of the absorption of the two betaines I and II with the parent base in various media shows the development of a new absorption band A in the higher wavelengths, which must be due to a different state of the molecule, apparently due to anhydro salt formation. The latter part of the curve in the region B the absorption of the two betaines shows a general bathochromic shift with a considerable rise in the extinction values. They show a sharp rise in absorption, instead of the

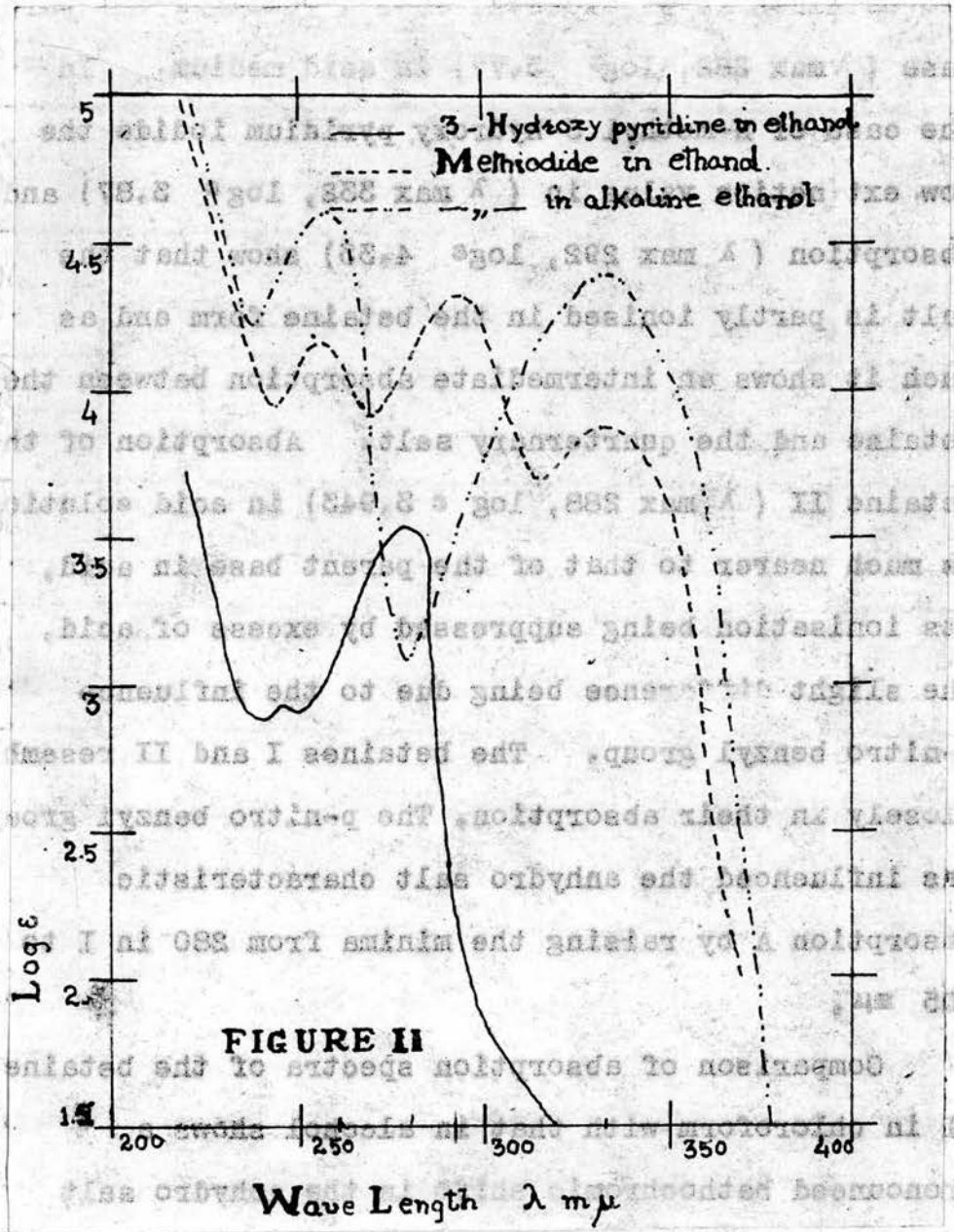

3-Hydroxy pyridine in ethanol
Methiodide in ethanol
" in alkaline ethanol
5
4.5
4
3.5
3
2.5
2
1.5
Log ε
200
250
300
350
400
Wave Length λ mμ

FIGURE II

absorption (λ max 280, logε 3.55) and (λ max 298, logε 3.63) shown by the parent base in neutral and alkaline media, respectively. The salts of the two betaines as is expected should resemble the parent base (λ max 282, logε 3.77) in acid medium. In the case of N-methyl 3-hydroxy pyridium iodide the low extinction values at (λ max 332, logε 3.87) and absorption (λ max 292, logε 4.33) show that the salt is partly ionised in the betaine form and as such it shows an intermediate absorption between the betaine and the quarternary salt. Absorption of the betaine II (λ max 288, log ε 3.943) in acid solution is much nearer to that of the parent base in acid, its ionisation being suppressed by excess of acid, the slight difference being due to the influence of the p-nitro benzyl group. The betaines I and II resemble each other closely in their absorption. The p-nitro benzyl group has influenced the anhydro salt characteristic absorption A by raising the minima from 280 in I to 305 mμ.

Comparison of the absorption spectra of the betaine II in chloroform with that in alcohol shows a pronounced bathochromic shift in the anhydro salt character A, which becomes much less in the region of lower wavelengths.

Thus there are two main features observed in the absorption spectra of anhydro salt derivatives of

3-hydroxy pyridine.(1) The presence of a new absorption band A in the higher wavelengths, not found in the parent base.(2) The absorption spectra in the lower wavelengths is only slightly altered, and is much the same as that of the parent base under identical conditions of the medium.

The solvents affect the anhydro salt spectra in two ways, which are in agreement with their betaine structure.

(1) Hydrogen bonding:- A hypsochromic shift in the anhydro salt characteristic maxima A in presence of ethanol as compared to that in chloroform is attributed to hydrogen bonding with the anionic oxygen which reduces the anhydro salt character of the molecule. This character further ceases to exist in presence of acids, when the hydrogen ion from the acids is permanently retained by the anionic oxygen destroying the anhydro salt character.

(2) Influence of polar solvents:- A batho-chromic shift of the anhydro salt character A is observed in chloroform, the polar solvent. In the polar solvents the anhydro salt character is partially neutralised, due to quenching of the effect of the charges on the anhydro salt molecule, by mutual binding of the opposite polarities of the solvent molecules. Such a deactivating influence of the anhydro salt character is comparatively less than

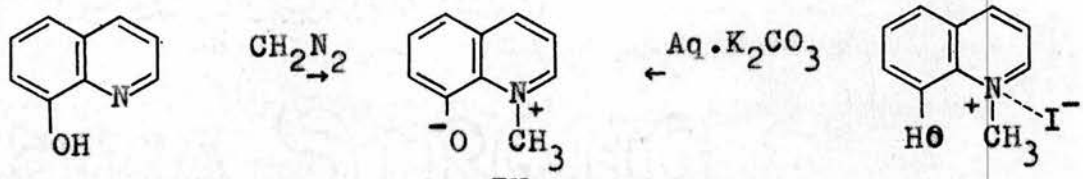
one due to hydrogen bonding.

A detailed study of the solvent effect is carried out on the 8-hydroxy quinoline betaine, which is more readily obtainable for experimental purposes.

N-methyl 8-hydroxy quinolium hydroxide anhydro salt IV

The betaine was prepared in the usual manner from its methiodide by the action of alkali, described in the experimental section.

G. Caronna and B. Sansone (Gazz. Chim. Ital. 1939, 69, 24-28) obtained a blue-red compound by the action of diazomethane on 8-hydroxyquinoline in ethereal solution, which correctly analysed for the betaine IV, but they failed to give any suitable formulation



IV

for this compound, which could explain its properties. Schenkel and Rudin (Helv. Chim. Acta, 1944, 27, 1456) assigned this compound, the betaineformula IV, to justify its polar character. Later J. Phillips and R. Keown (J. Amer. Chem. Soc.,1951, 73, 5483) confirmed the dipolar character and the formula IV of this compound, by its spectrocopic analysis in solutions of different pH. They called this compound as diazoxine, which was identical with the

betaine derived by us, by the above mentioned method. This was further supported by the identical absorption spectra of these two compounds obtained through different methods.

A study of the colour but not the spectra of phenol betaines of the quinoline series in different solvents was first taken up by W. Schneider (Ber. 1941, 74, 471) (Amer. Chem. Abs. 1941, 5115,1) but the work remained incomplete due to his death.

N-methyl 8-hydroxy quinolinium hydroxide anhydro salt is selected as the representative phenol betaine of the quinoline series, to investigate the solvent effect upon their absorption spectra in ultra violet and visible region.

High colour of the anhydro salts of these types is a special feature explained by their dipolar character. The pyridinium cation, and the anionic oxygen are in different rings in all the cases (cf. 3- hydroxy pyridine betaine).

Standard solutions of 8-hydroxy quinoline and the betaine IV, were prepared in ethanol. To 1 ml. of each solution 2 mls. of 5% standard ethanolic hydrochloric acid was added, and both were separately made up to 10 mls. Their spectra in the visible region showed no absorption, while the ultra violet absorption in both the cases, table II, as was expected was the same. The close resemblance of the

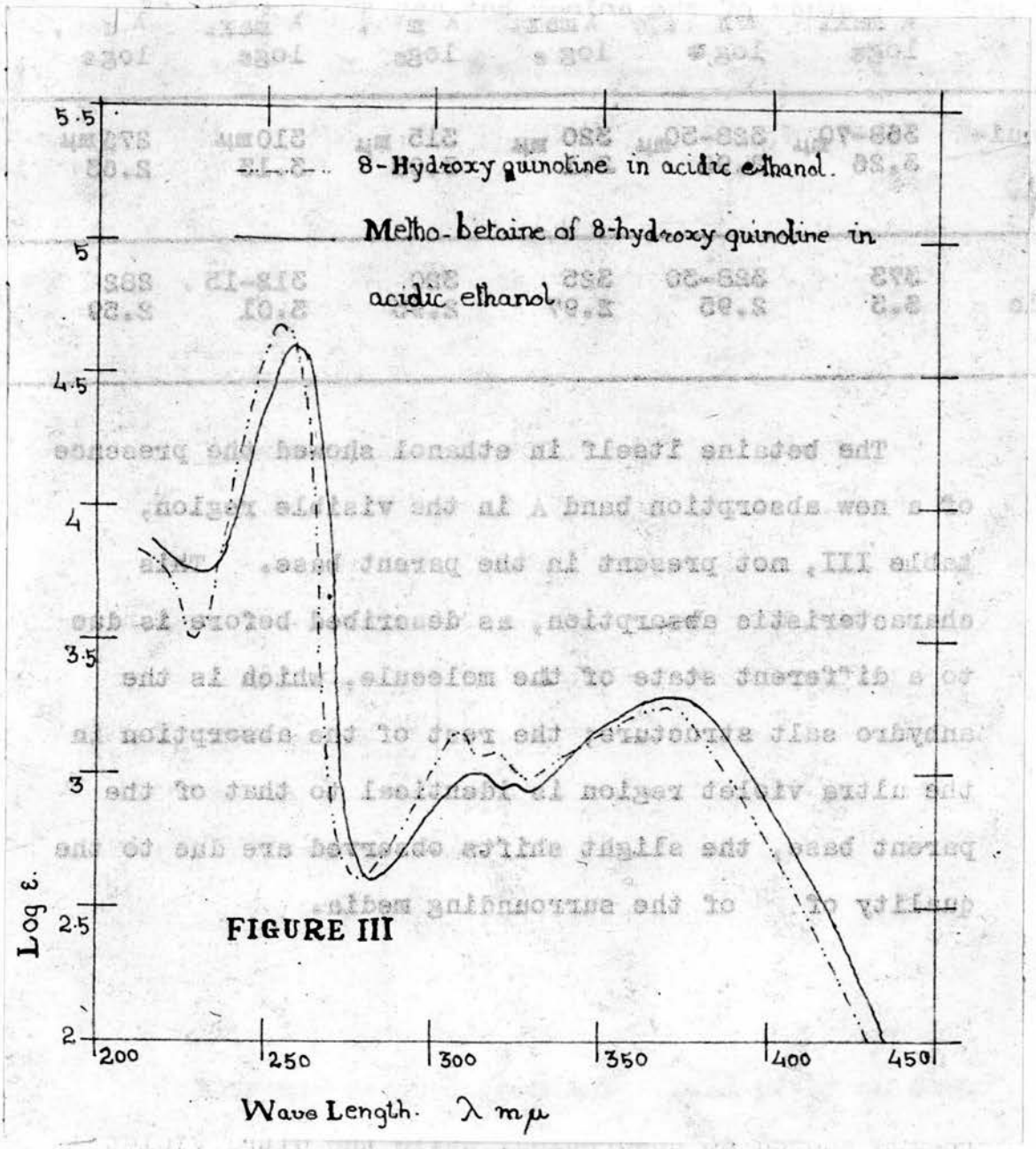

8-Hydroxy quinoline in acidic ethanol.
Metho-betaine of 8-hydroxy quinoline in acidic ethanol
5.5
5
4.5
4
3.5
3
2.5
2
Log ε.
200
250
300
350
400
450
Wave Length. λ mμ

FIGURE III

two curves in figure III, shows that the salts of the parent base and the betaine are of identical structure.

Table II.

ompound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε
ydroxy qui-line in anol+HCl.	368-70 mμ 3.26	328-30 mμ 2.98	320 mμ 3.1	315 mμ 3.08	310 mμ 3.13	276 mμ 2.63	255 mμ 4.68	250 mμ 3.49
taine IV ethanolic ..	373 3.3	328-30 2.95	325 2.97	320 2.95	312-15 3.01	282 2.59	258-59 4.61	254-5 3.74

The betaine itself in ethanol showed the presence of a new absorption band A in the visible region, table III, not present in the parent base. This characteristic absorption, as described before is due to a different state of the molecule, which is the anhydro salt structure; the rest of the absorption in the ultra violet region is identical to that of the parent base, the slight shifts observed are due to the quality of pH of the surrounding media.

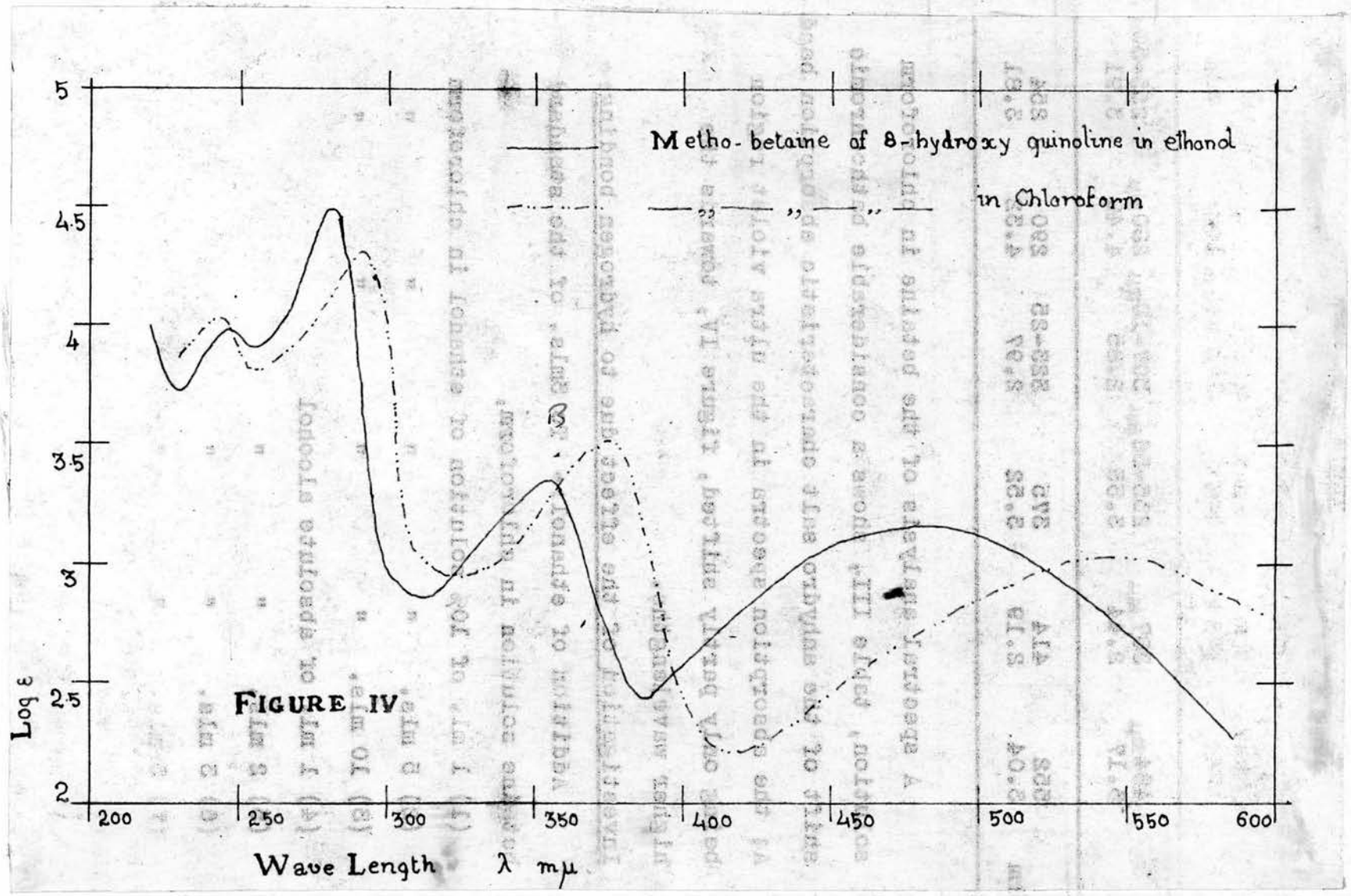

Metho-betaine of 8-hydroxy quinoline in ethanol
" " " in Chloroform
Log ε
5
4.5
4
3.5
3
2.5
2
200
250
300
350
400
450
500
550
600
Wave Length λ mμ

FIGURE IV

Table III.

A

ompound	λmax. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
etaine IV n ethanol	484 mμ 3.17	387 mμ 2.44	255-56 mμ 3.35	307-10 mμ 2.85	280 mμ 4.49	255-56 mμ 3.91	245-46 mμ 3.97
etaine IV n chloroform	552 3.04	414 2.19	375 3.52	323-25 2.97	290 4.32	254 3.81	242 4.2

A spectral analysis of the betaine in chloroform solution, table III, shows a considerable bathochromic shift of the anhydro salt characteristic absorption band A; the absorption spectra in the ultra violet region being only partly shifted, figure IV, towards the higher wavelengths.

Investigation of the effect due to hydrogen bonding:-

Addition of ethanol:- To 3mls. of the standard betaine solution in chloroform,

(1) 1 ml. of 10% solution of ethanol in chloroform
(2) 5 mls. " " " "
(3) 10 mls. " " " "
(4) 1 ml. of absolute alcohol
(5) 2 mls. " "
(6) 3 mls. " "
(7) 5 mls. " "
(8) 10 mls. " "
(9) 20 mls. " "
(10) 40 mls. " "

(11) 60 mls. of absolute alcohol.

(12) 97 mls. of absolute alcohol, respectively, were added. The solution in each case was made up to 100 mls. with chloroform, and their absorption spectra were measured in the visible and ultra violet region. Table IV shows the positions of maximum absorption, taken at different concentrations of alcohol.

Table IV.

Mls. of alcohol 100 mls.	Moles of alcohol per litre	λmax. in the visible region	Mean $\lambda_{max.}$	λmax. in the ultra violet region.
None	None	560-44 mμ	552 mμ	276-5 mμ
0.1	0.0174	554-44	549	375
0.5	0.087	550-40	545	374
1.0	0.174	540-37	538.5	371
1.0	0.174	545-39	542	372
2.0	0.348	535-30	532.5	369
3.0	0.522	530-25	527.5	367
5.0	0.870	523-15	519	365
10	1.74	515-12	513.5	362
20	3.48	507-499	503	360
40	6.96	500-490	495	358
60	12.44	492-88	485	356

Addition of alcohol, thus, produces a hypsochromic shift, which is more pronounced in the visible region

than in the ultra violet. The increase in shift is proportional to the concentration of alcohol. The greater is the concentration of alcohol the greater is the value of shift. This shift became practically constant after the addition of 20 to 40 mls. of alcohol, attaining a maximum value at 100% concentration when the position of λ max. is $484_{m\mu}$.

The shift, $\Delta \lambda$max, in the position of maximum in the visible region, due to addition of alcohol, from that in pure chloroform, is plotted against the concentration of alcohol in moles/litre. Figure V. The gentle slope of the curve shows a gradual shift in the position of maxima.

Addition of O-nitrophenol:- A 10% solution of recrystallised O-nitrophenol in chloroform was prepared. Portions of 1, 5, 10 and 20 mls. of this solution, were added to 3 mls. of standard betaine solution in chloroform. Each of these was individually made up to 100 mls. with chloroform. Since the solvent also absorbed in the visible region, standards of the same concentration of phenol, with no betaine solution in them, were used in the balancing cell, to neutralise the effect of the solvent.

Table V gives the positions of absorption maxima in the visible region, for the various solutions, with different concentrations of o-nitro phenol.

$\Delta \lambda$max is the shift in the position of absorption

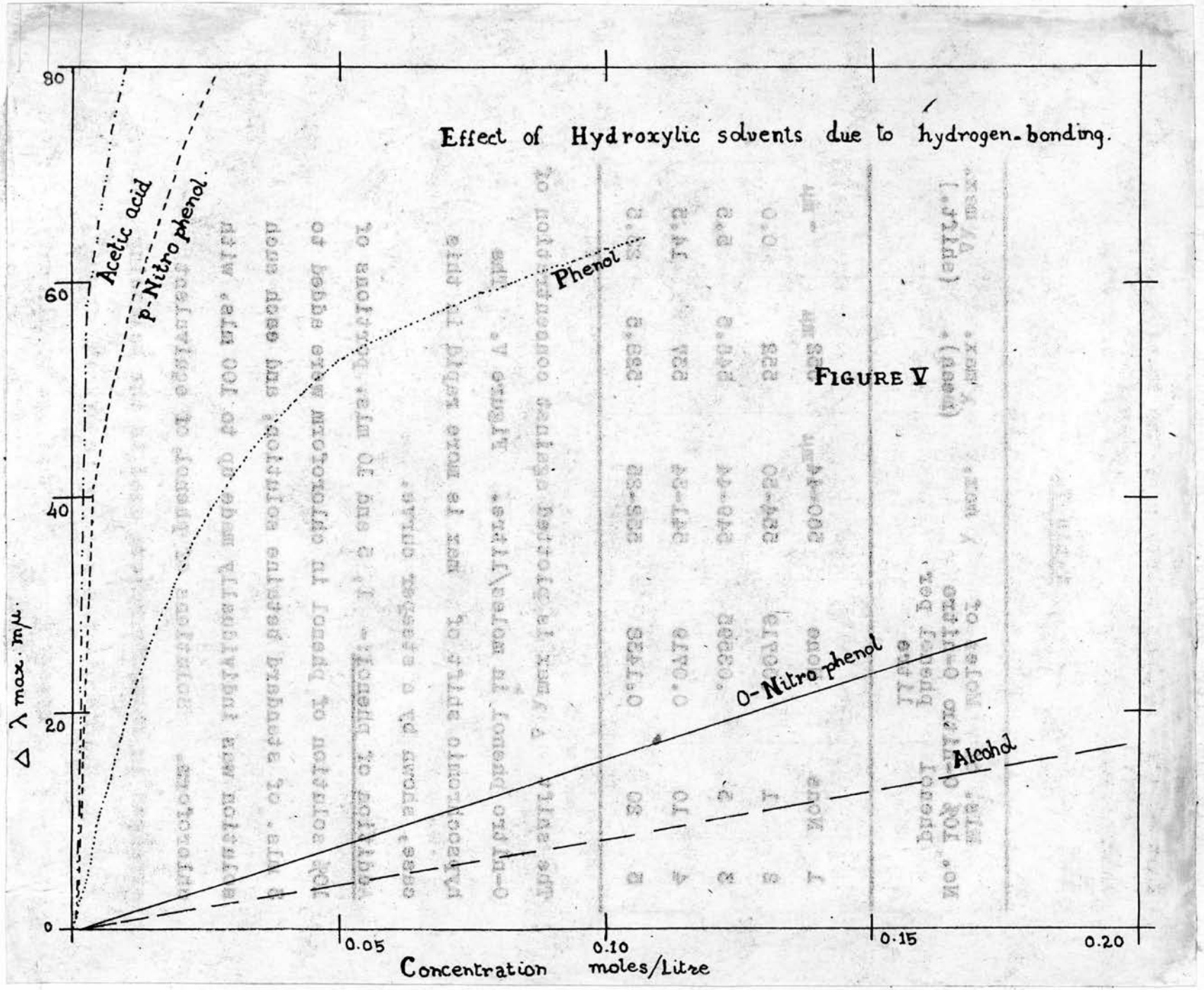

Effect of Hydroxylic solvents due to hydrogen-bonding.
Acetic acid
p-Nitro phenol.
Phenol
O-Nitro phenol
Alcohol
80
60
40
20
0
Δ λ max. m/μ.
0.05
0.10
0.15
0.20
Concentration moles/Litre

FIGURE V

maxima due to the addition of 0-nitro phenol, from that of the original solution of the betaine in chloroform.

Table V.

No.	Mls. of 10% 0-nitro phenol	Moles of 0-nitro phenol per litre	λ max.	λ max. (mean).	Δλ max. (shift.)
1	None	None	560-44mμ	552 mμ	- mμ
2	1	.00719	554-50	552	0.0
3	5	.03595	549-44	546.5	5.5
4	10	0.0719	541-34	537	14.5
5	20	0.1438	532-25	528.5	23.5

The shift $\Delta \lambda$max is plotted against the concentration of 0-nitro phenol in moles/litre. Figure V. The hypsochromic shift of λ max is more rapid in this case, shown by a steeper curve.

Addition of phenol:- 1, 5 and 10 mls. portions of a 10% solution of phenol in chloroform were added to 3 mls. of standard betaine solution, and each such solution was individually made up to 100 mls. with chloroform. Solutions of phenol, of equivalent strength in chloroform were used in the balancing cell, to counteract the absorption effect of the solvent. A hypsochromic shift of the wavelengths of maximum absorption in the visible region, was

again observed. Table VI gives the positions of maximum absorption by different solutions under different concentrations of phenol, together with the shift $\Delta \lambda$ max suffered by them.

Table VI.

Se. No.	Mls. of 10% phenol	Moles of phenol per litre	λ max.	λ max. (mean)	$\Delta\lambda$ max. (shift)
1	None	None	560-44 mμ	552 mμ	- mμ
2	1	.01064	522-14	518	34
3	5	.0532	504-493	498	54
4	10	.1064	494-84	489	63

A curve was plotted between $\Delta \lambda$ max and the concentration of phenol in moles/litre. Figure V. A much steeper shift is observed with the addition of phenol. The shift being proportional to the concentration of phenol.

Addition of p-nitro phenol:- Since p-nitro phenol is very insoluble in chloroform; standard solutions were prepared by dissolving 50 mgs. and 100 mgs. of recrystallised p-nitro phenol, respectively, into 3 mls. of standard betaine solution, and both were made up individually to 100 mls., with chloroform. For securing a counterbalance for absorption by the solvent, a solution of p-nitro phenol of the same concen-

tration was used in the balancing cell. A hypsochromic shift in the absorption maxima in the visible region was again observed. Table VII gives the wavelengths of maximum absorption in the visible region by the two solutions of different concentration of p-nitro phenol; together with the shift $\Delta\lambda$ max suffered by them.

Table VII.

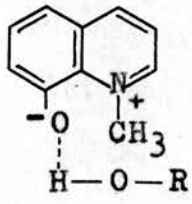
Se. No.	Mgs. of p-nitro phenol	Moles of p-nitro phenol/ litre.	λ max.	λmax. (mean)	$\Delta\lambda$max. (shift)
1	None	None	560-44 mμ	552 mμ	- mμ
2	50	0.0036	502-89	495.5	56.5
3	100	0.0072	490-81	485.5	66.5

A curve was plotted between $\Delta\lambda$ max, the shift in absorption maxima, and concentration of p-nitro phenol in moles/litre. A much more steep shift of absorption maxima to lower wavelengths is shown by the sharp rise of the curve along the axis of Y. Figure V.

Addition of Acids:- Addition of acids like glacial acetic acid, hydrochloric acid etc., destroys the anhydro salt character, for there is not only a strong hydrogen bonding with the cationic oxygen, but also there is the neutralisation of the charge

upon the nitrogen cation, and thus in that state as is expected the spectra closely resembles that of the parent base in acid. Figure III. Absence of the absorption in the visible region, shows the disappearance of anhydro salt character.

Inference:- From the above experiments it is observed that for a given concentration of the hydroxylic solvent, a greater hypsochromic shift in the position of λmax occurs, depending upon the capability of the hydroxy compound to donate a hydrogen atom, to the anionic oxygen of the betaine. This influence of decrease in absorption of the anhydro salt character A, due to hydroxylic compounds from higher to lower wavelengths, Figure V, is in the order of (p-nitro phenol > phenol > O-nitrophenol > alcohol) according to their readiness for hydrogen bonding.



A hypsochromic shift, on addition of a hydroxylic solvent is therefore due to the phenomenon of hydrogen bonding with the anionic oxygen. This phenomenon tends to reduce the anhydro salt state of the molecule, thereby bringing about the decrease in the anhydro salt character A, by shifting it to lower wavelengths. In presence of acids, this character

ceases to exist, because the hydrogen donated by the acid is permanently retained by the anion, and further losing the anhydro salt character by the neutralisation of the charge of the cation.

Influence of polar solvents:- To study the effect of polar solvents of different dipole moments, upon the anhydro salt character A, absorption maxima of the betaine in the visible region were measured, in the various solvents having no tendencies for hydrogen bonding.

1 ml. of standard solution of betaine was diluted to 25 mls. with (1) acetonitrile (2) acetone (3) nitrobenzene (4) benzene and (5) carbon tetrachloride. Table VIII gives the wavelengths of maximum absorption in visible region, in different solvents, placed in the order of decreasing dipole moments.

Table VIII.

Solvent	$\lambda^{max.}_{(mean)}$.
Acetonitrile	506 mμ
Acetone	525
Nitrobenzene	535
Chloroform	550
Benzene	568
Carbontetrachloride	579

With the decrease of dipole moments of the solvent, there is observed a bathochromic shift of the anhydro salt characteristic absorption maximum, which attains its highest maximum value in the non polar solvent (carbon tetra chloride); a medium in which the anhydro salt character is fully displayed, unaffected by the polarity or hydrogen bonding phenomenon.

Such a decrease in the absorption waveband with the increase of dipole-moment of the solution is ascribed to the fact that in polar solvents, the anhydro salt character is partly neutralised, due to quenching of the effect of the charges on the betaine molecule, by their association with opposite polarities of the solvent molecules.

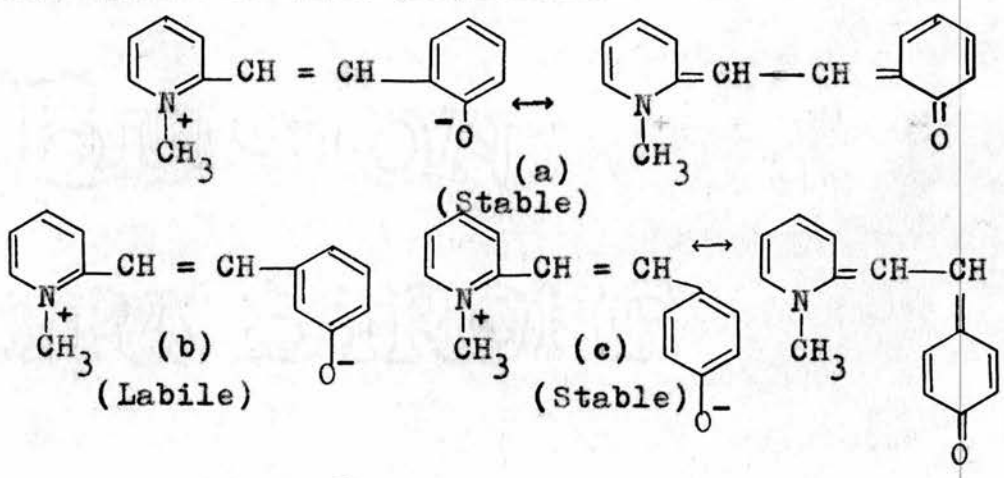
This deactivating influence is of lesser intensity than the hydrogen bonding, as shown by the absorption maxima in ethanol (λmax. 484), which is in much lower wavelengths than the above mentioned polar compounds. In a non polar solvent like cyclohexane or carbon tetra chloride, the anhydro salt character is at its peak, (being unaffected by the influences like hydrogen bonding or polarity) shown by its absorption maxima in the highest wavelengths.

An important feature about the absorption spectrum of the betaine in carbon tetra chloride or cyclo-hexane, is that the solution of betaine in these was in a metastable state, and consequently their spectra

was taken as soon after preparation as possible, because the crystals of the betaine separated out after a short time.

To notice the effect of conjugation and the various resonant forms in which the anionic centre is situated, with respect to the nitrogen cation; some more simple betaines were made and studied, from the substituted quinolines and pyridines through their methiodides by their similar treatment with alkali.

N-methyl (O-,m- and p-hydroxy phenyl) stilbazolium hydroxide anhydro salts:- V (a), (b) and (c). A detailed method of their preparation



V

is given in the experimental section. All the three betaines are highly coloured. The betaine V (a), and V (c), are more stable than the V (b), due to their capability of existence in two resonant forms, (1) the betaine (2) the pyridone quinone. There is

a preponderance of the form (1) over (2), because it accounts more readily for their polarity and high colour. Only the betaine V (a) could be isolated in crystalline form, while the other two proved elusive, and as such their absorption spectra were studied through their methiodides in alkaline medium. These betaines resembled closely the 8-hydroxy quinoline betaine. Thus they were highly basic, and formed colourless salts with acids. Their spectral properties in various media are analogous to the 8-hydroxy quinoline betaine, which are in agreement with their anhydro salt character. Table IX gives the absorption spectra of the methiodide, of (a), (b) and (c) in ethanol and alkaline ethanol.

Table IX

A

ethiodide of the Compound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε
(a) In ethanol	- mμ	- mμ	358-60 mμ 3.98	318-20 mμ 3.9	295-99 mμ 3.96	258-60 mμ 3.81
(a) in alkaline ethanol	494 4.36	395 3.43	348 4.23	288 3.47	250 4.12	242 4.06
(b) in ethanol	-	-	345 4.25	295 3.77	276 3.84	254 3.71
(b) in alkaline ethanol	425-40 - inflection - 3.6		360-62 4.22	303 3.74	268 3.98	260 3.97
(c) in ethanol	-	-	372 4.16	320 3.61	286 4.01	264 3.95
(c) in alkaline ethanol	494-96 4.44			328 3.26	285-86 3.84	252 3.57

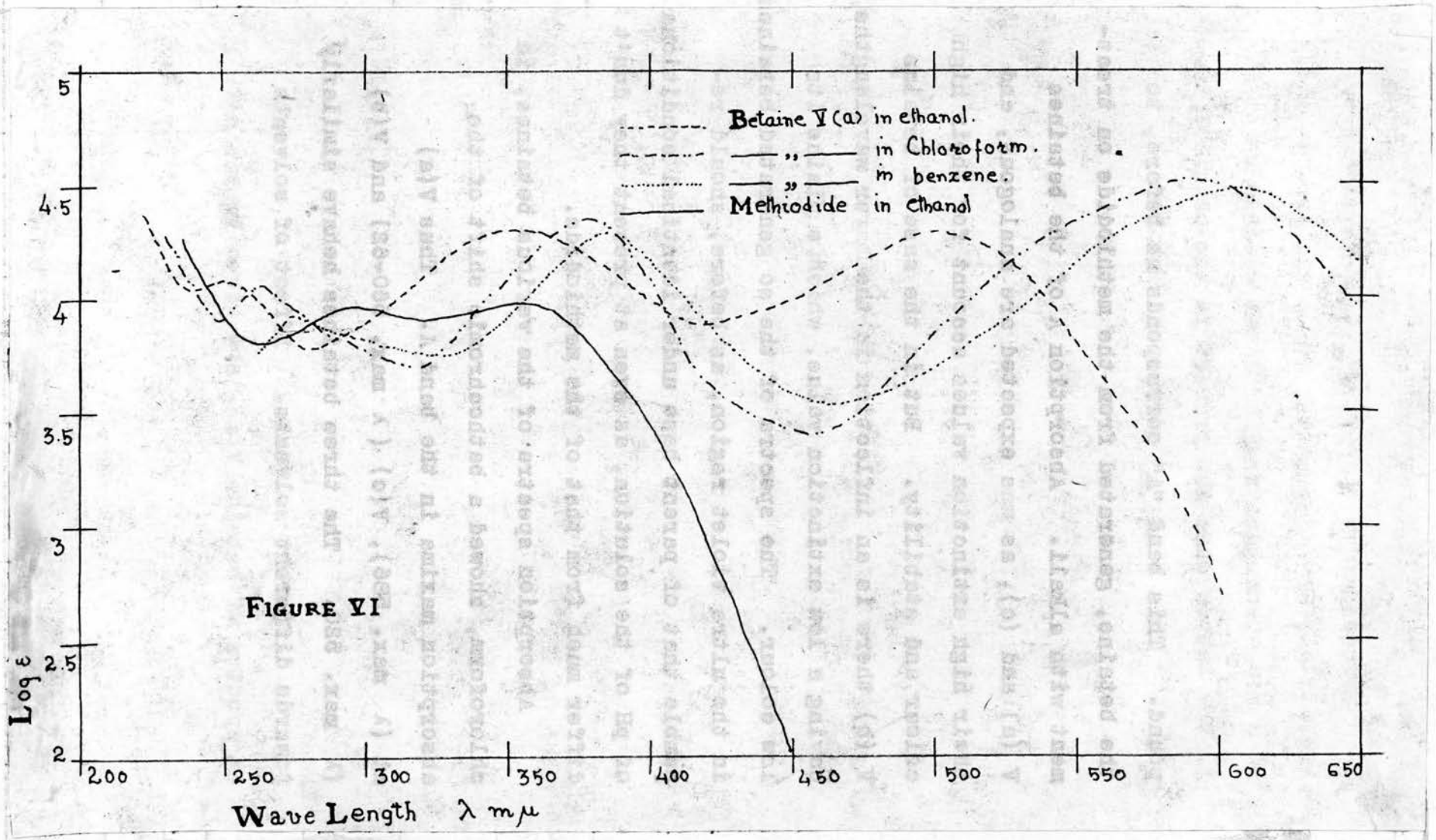

Betaine V (a) in ethanol.
,, in Chloroform.
,, in benzene.
Methiodide in ethanol
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
500
550
600
650
Wave Length λ mμ

FIGURE VI

Comparison of the spectra of the methiodides in neutral and alkaline media, shows the development of a new absorption band A in the visible region in the latter case, not present in the original compound. This band "A" corresponds as before, to the betaine, generated from the methiodide on treatment with alkali. Absorption A of the betaines V (a) and (c), as was expected are analogous, and their high extinction values account for their high colour and stability. But in the case of betaine V (b) there is an inflection in the longer wavelengths, having a low extinction value, which explains its low colour. The spectra of the so generated betaines in the ultra violet region, as before, should resemble that of parent base under identical conditions of pH of the solution, as even at present they don't differ much from that of the methiodide.

Absorption spectra of the various betaines, in chloroform, showed a bathochromic shift of the absorption maxima in the band A. Thus V(a) absorbed at (λ max. 586), V(c) (λ max. 560-62) and V(b) (λ max. 520. The three betaines behave similarly towards different solvents. Effect of solvents on spectra of betaine V(a), are given in table X.

Table X.

A

etaine V (a)	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε
n chloroform	586 mμ 4.56	458-60 mμ 3.43	378-79 mμ 4.35	320 mμ 3.72	264 mμ 4.07	248 mμ 3.92
n alcohol	494 4.3	419-20 3.89	352 4.31	280 3.77	250 4.1	240 4.04
n benzene	598 4.49	460 3.53	385-87 4.25	328 3.73	276 3.95	-

An examination of the figure VI and table X shows that there is a hypsochromic shift in anhydro salt characteristic absorption A, in ethanol as solvent (hydrogen bonding), and a bathochromic shift of the same, in benzene as solvent (polar effect) as compared to chloroform solution. The remaining part of the curve shows a slight hypsochromic or a bathochromic shift, according to the solvent used.

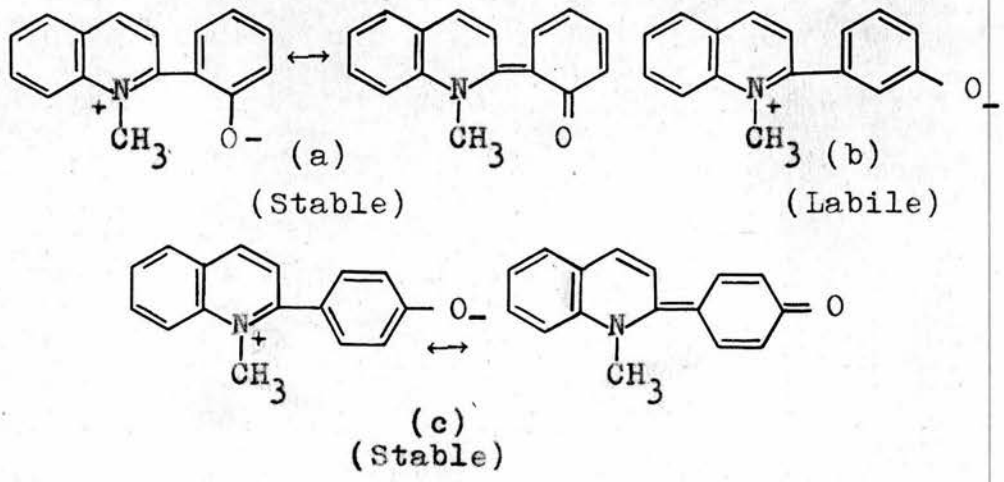
Thus the solvent effect on these betaines due to hydrogen bonding and polar effect are just the same as the 8-hydroxy quinoline betaine.

These betaines were also found to be thermochromic. Thus a dilute solution of V (a) in chloroform at room temperature was purple; this changed to blue (bathochromic shift) in boiling solution and then turned orange red (hypsochromic shift) at the temperature of solid CO_2/acetone.

This phenomenon is ascribed to the fact that with the application of heat, association of the betaine molecules with the polar solvent molecules is reduced, resulting in the development of anhydro salt character A, in the higher wavelengths; which shifts to lower wavelengths, at low temperature when chloroform molecules will have a high capacity for association, and at room temperature an intermediate capacity.

2-(O-, m- and p-hydroxy phenyl) quinolinium hydroxide anhydro salts:- VI (a), (b), and (c).

First the parent bases were prepared by condensation of o-aminobezaldehyde with o-, m- and p-hydroxy acetophenone. The resulting bases agreed in their melting points with the same material, previously made by different methods. Their methiodides were made, to synthesise



VI

betaines from them. (see experimental). 2-(o-hydroxy phenyl) quinolinium iodide failed to give

any colour with alkali probably due to pseudo base formation. The remaining two, gave coloured betaines which in their properties and behaviour in solvents, agreed with their anhydro salt form. Only the betaine VI (c) could be isolated in crystalline form. These anhydro salts are highly basic and give colourless salts with acids. They have intense colour, and have great affinity for water. Their stability is dependent upon the number of mesomeric forms in which they can exist.

A critical study of the absorption spectra of the iodides of VI (b) and (c) in neutral and alkaline ethanol compared with the parent base in identical conditions is given below.

Table XI.

A

Compounds allied to (b)	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
arent base in thanol	mμ	mμ	327 mμ 3.97	305 mμ 3.88	254 mμ 4.52	236 mμ 4.31	mμ
ethiodide of above n ethanol			328-30 4.1	292 3.58	266-68 3.85	258 3.81	240 4.6
ase in acidic thanol			340 4.12	290-92 3.52	264 4.25		
ethiodide in lkaline ethanol	450 2.66	390 2.36	(328-32 inflec- tion 3.79)		308 3.84	282 3.6	234 4.62
ase in lkaline ethanol			325 3.91	320 3.85			234 4.53

Table XII (for compounds allied to VI (c)).

A

Compound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
ent base in anol	mμ	mμ	335 mμ 4.05	315 mμ 3.86	270-72 mμ 4.34	246 mμ 4.08	mμ
hiodide in anol			335-37 4.01	312 3.87	270 4.2	258 4.14	
ent base in dic ethanol			378 4.33	313 3.45	290-92 3.98	275 3.93	
hiodide in aline ethanol	478-80 4.04	420 3.7	373 4.02	340 3.85	315 4.11	294 4.0	282 4.02
e in aline ethanol			372 4.22	338 3.88	318 4.12	295 3.99	278 4.06

A glance at the table X and XII shows that the spectrum of the methiodide is intermediate between that of the parent base in neutral and alkaline media. The spectrum of the betaines VI (b) and VI (c) obtained from the methiodides on alkaline treatment, again show an anhydro salt characteristic absorption, missing in the parent base. The remaining part in the ultra violet absorption of the betaines is analogous to that of the parent base in alkaline medium.

The low absorption characteristics of the betaine VI(b) (λ max. 450, log ε 2.66) as compared

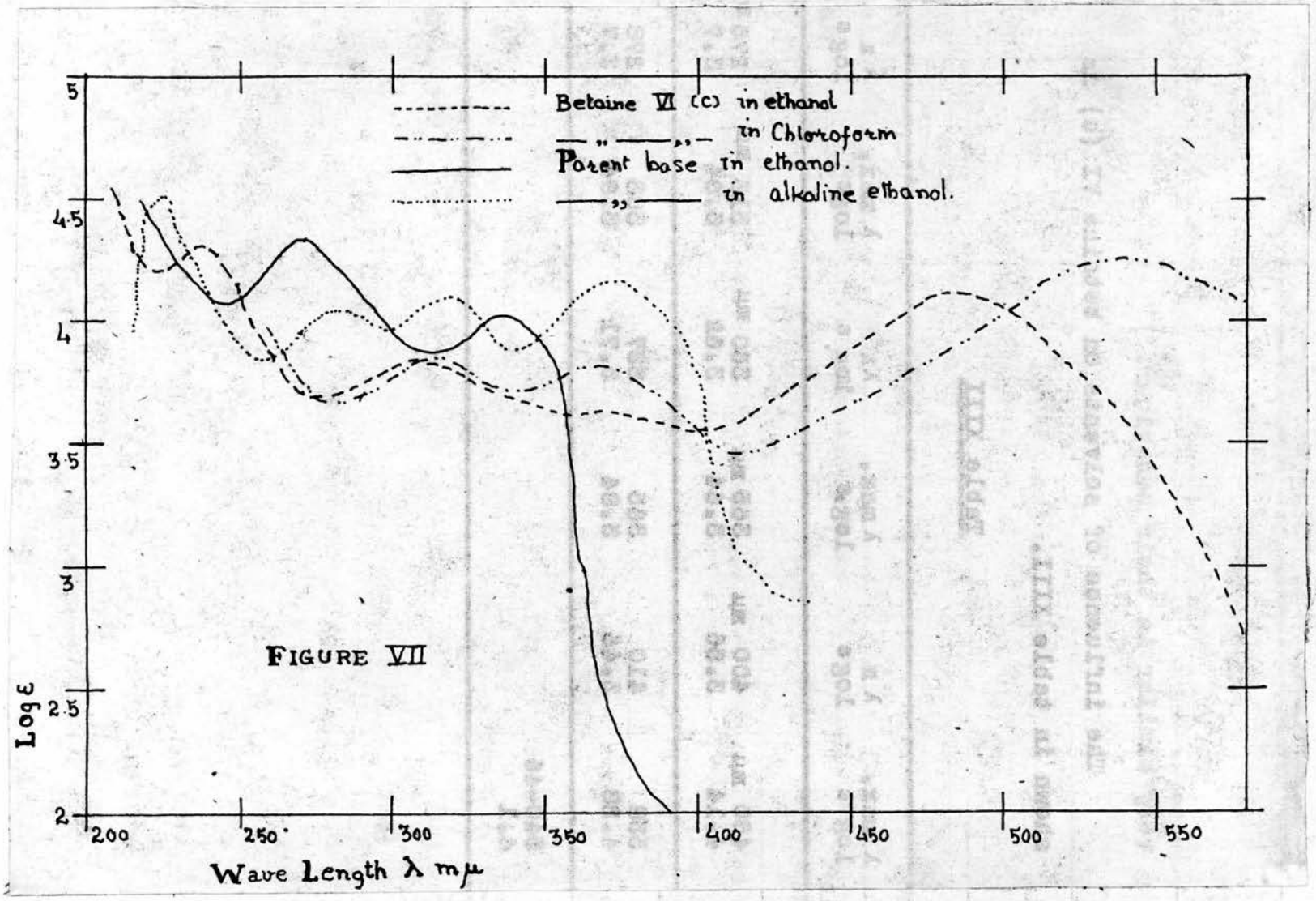

Betaine VI (c) in ethanol
" " " in Chloroform
Parent base in ethanol.
" " in alkaline ethanol.
Log ε
5
4.5
4
3.5
3
2.5
2
200
250
300
350
400
450
500
550
Wave Length λ mμ

FIGURE VII

to VI (c) (λ max. 478-80, log ε 4.04), accounts for low colour and stability of the former, which is attributed to its existence in only one mesomeric anhydro salt form. Otherwise the two betaines are very similar in their behaviour.

The influence of solvents on betaine VI (c) is shown in table XIII.

Table XIII

A

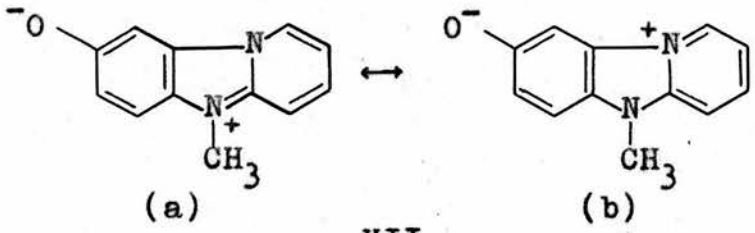
ivent	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
anol	480 mμ 4.14	400 mμ 3.56	365 mμ 3.64	360 mμ 3.62	313 mμ 3.84	275 mμ 3.7	238 mμ 4.32
oroform	538 4.28	410 3.46	365 3.84	337 3.71	308 3.84	278 3.7	266 3.8
zene	540-46 4.1						

The close resemblence of the spectrum of the betaine in ethanol to that of the methiodide in alkaline medium, confirms its formation from the methiodide on alkaline treatment. Figure VII shows the hypsochromic shift of the anhydro salt character, on addition of ethanol (hydrogen bonding) and a bathochromic shift of the same on using solvents of decreasing dipole moments (also see table XIII). The absorption in the ultra violet region is only slightly shifted.

To study the effect of the presence of two nitrogen atoms in the system capable of acting as cation through resonance, and an oxygen atom as an anion. The following betaine was studied:

N-methyl-6:hydroxy 1'-2'-1-2 Pyridobenziminazolium hydroxide anhydro salt:- VII

The betaine VII was prepared from the methiodide by treatment with silver carbonate in alcohol solution; but did not analyse correctly due to its immense capacity for hydration. This betaine could also be made from the parent base on treatment with diazomethane (cf. 8-hydroxy quinoline betaine)



(a) (b)

VII

Structurally this betaine can be contrasted with

Besthorn's red (see introduction) with positive charge resonating between two nitrogen atoms and a negative charge residing on oxygen. The betaine is highly basic and gives colourless salts with acids. It is very susceptible to moisture, and decomposes on keeping for a long time.

A comparative study of the absorption spectrum of the betaine and the parent base in identical conditions of the solvents is given in table XIV.

Table XIV.

A

pound	λmax. log ε	λmin. log ε	λmax. log ε	λ min. log ε	λ max. log ε	λmin. log ε	λmax. log ε
ent base ethanol	mμ	mμ	360 mμ 3.78	320 mμ 3.24	300 mμ 3.76	296 mμ 3.67	248 mμ 4.5
aine in anol	413-15 3.82	332 3.47			272 4.32	260 4.29	242 4.46
ent base alkaline anol	405 3.87	333-35 3.16			268-70 4.49	250 4.34	242 4.36
e in acid- ethanol			358 3.94	308 4.33	292 3.71	280 3.65	238 4.17
aine in oroform	486 3.83	399 3.51	350-53 3.8	338-42 3.79	298 4.13	284 4.07	253 4.31

Development of the band "A" on addition of alkali to the parent base, shows the formation of

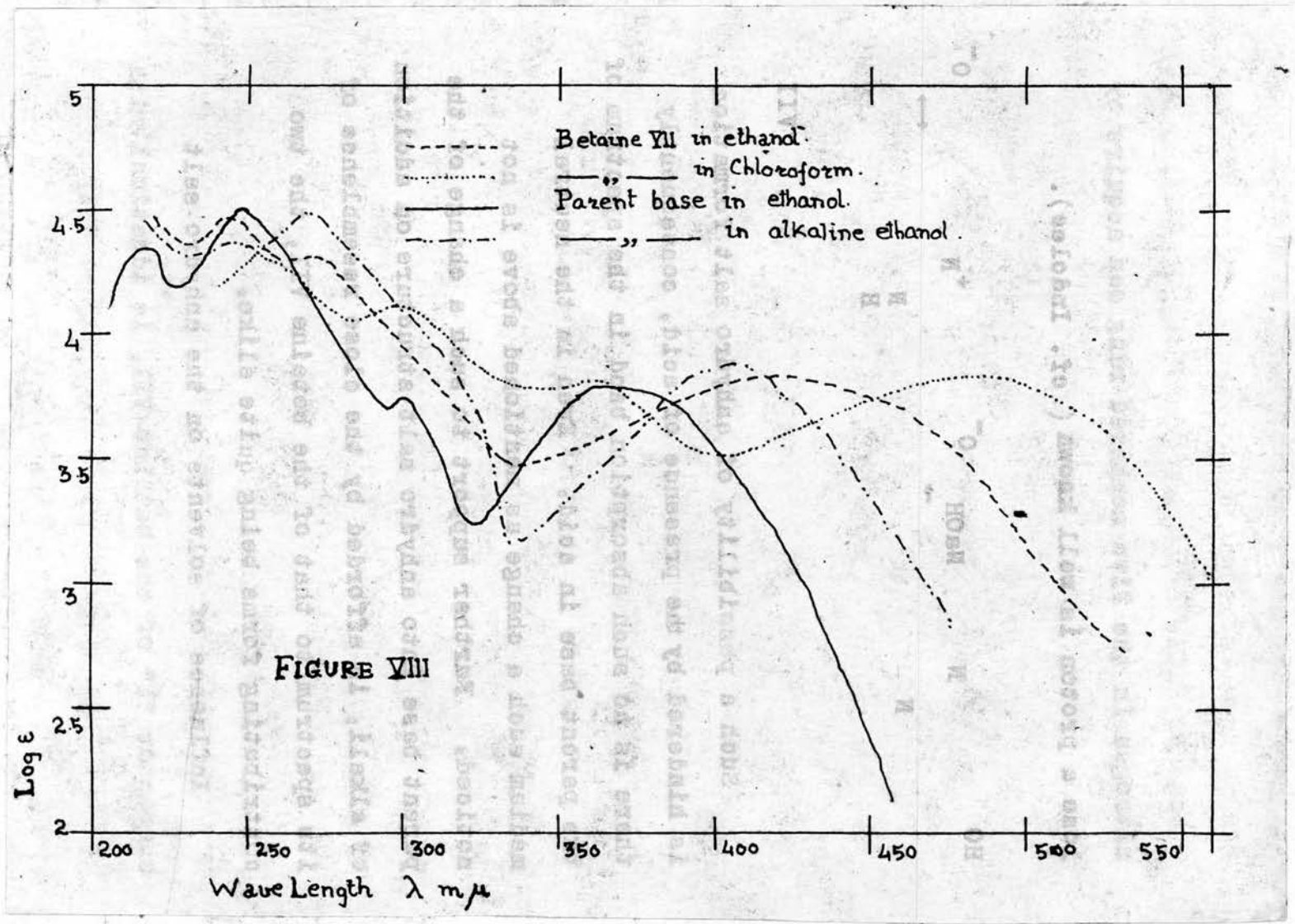
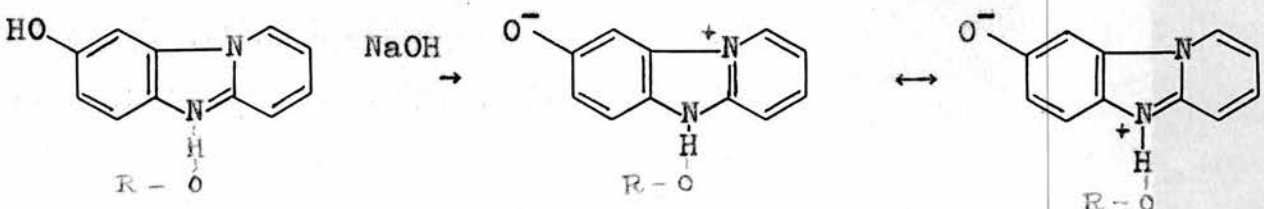

Betaine VII in ethanol.
—— ,, —— in Chloroform.
Parent base in ethanol.
—— ,, —— in alkaline ethanol.
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
500
550
Wave Length λ mμ

FIGURE VIII

anhydro salt structure, which is explained by the fact that when the base is treated with alkali the proton from oxygen is lost leaving the anhydro salt structure VIII. The readiness with which the nitrogen in the five membered ring can acquire or lose a proton is well known (cf. Indoles).



VII$_I$

Such a possibility of anhydro salt formation is hindered by the presence of acid, consequently there is no such absorption band in the spectrum of the parent base in acid. Even in the neutral medium such a change as mentioned above is not noticed. Further support to such a change of the parent base into the anhydro salt structure on addition of alkali, is afforded by the close resemblence of its spectrum to that of the betaine VII, the two contributing forms being quite alike.

Influence of solvents on the anhydro salt character "A" of the betaine VII, is identical with the betaines discussed before. Figure VIII shows a bathochromic shift of the absorption band A together with general shift of the curve in the ultra violet region to the right hand side, in chloroform.

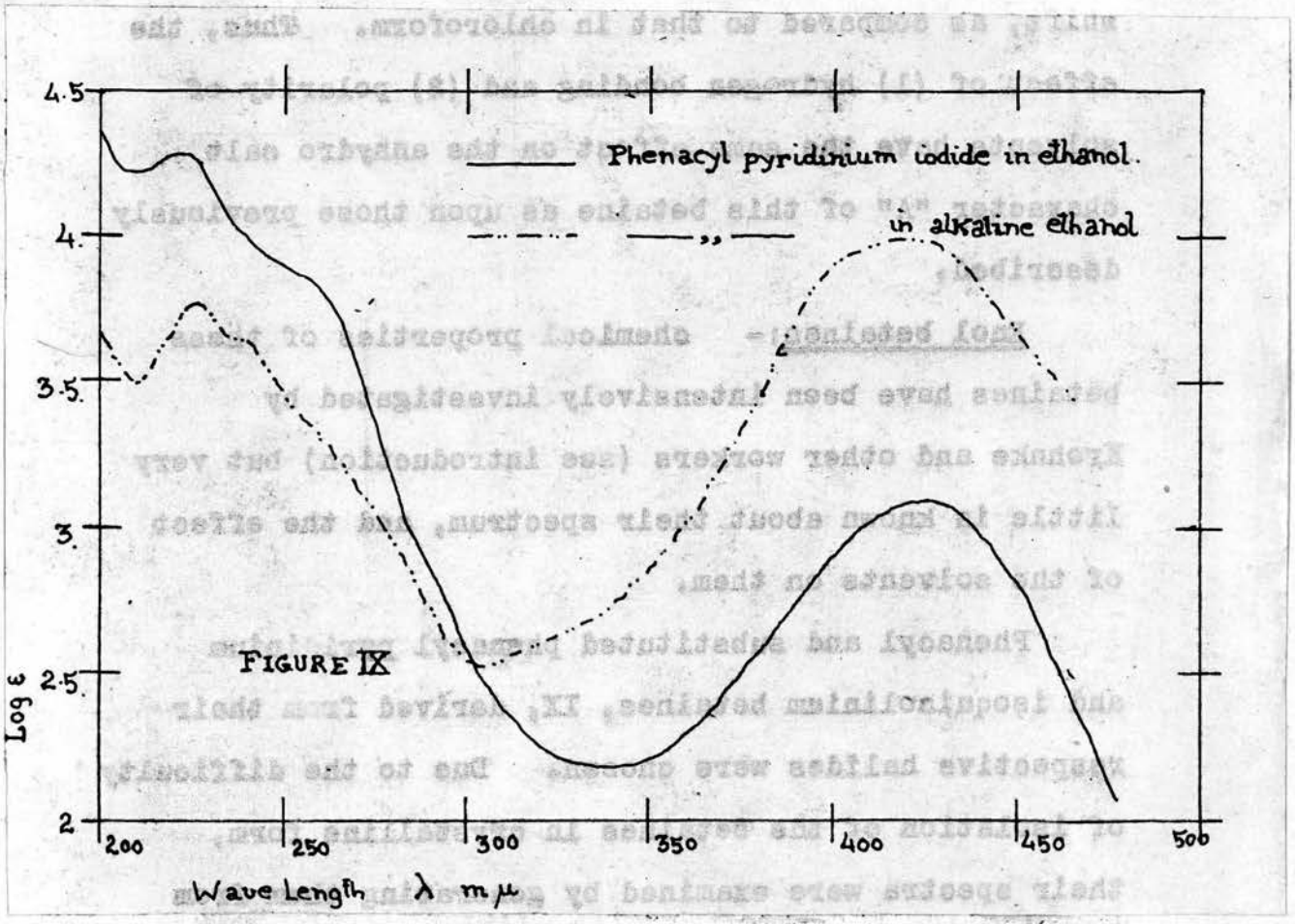
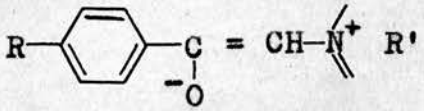

4.5
4
3.5
3
2.5
2
Log ε
Phenacyl pyridinium iodide in ethanol.
,, in alkaline ethanol
200
250
300
350
400
450
500
Wave Length λ mμ

FIGURE IX

In solvents of lower dipole moments e.g. benzene, in which the compound is insoluble and gave a purple meta stable solution, (the spectrum of which could not be taken as the betaine separated out immediately) but from colour an absorption in higher wavelengths is signified. In alcohol we observe a hypsochromic shift, as compared to that in chloroform. Thus, the effect of (1) hydrogen bonding and (2) polarity of solvents have the same effect on the anhydro salt character "A" of this betaine as upon those previously described.

Enol betaines:- The chemical properties of these betaines have been intensively investigated by Krönhnke and other workers (see introduction) but very little is known about their spectra, and the effect of the solvents on them.

Phenacyl and substituted phenacyl pyridinium and isoquinolinium betaines, IX, derived from their respective halides were chosen. Due to the difficulty of isolation of the betaines in crystalline form, their spectra were examined by generating them from their corresponding halides in alkaline alcohol



IX

(a) R = H
R'= Pyridine nucleus.
(b) R = CH_3
R'= Pyridine nucleus.
(c) R = Br
R'= Pyridine nucleus.
(d) R = Br
R'= Isoquinoline nucleus.

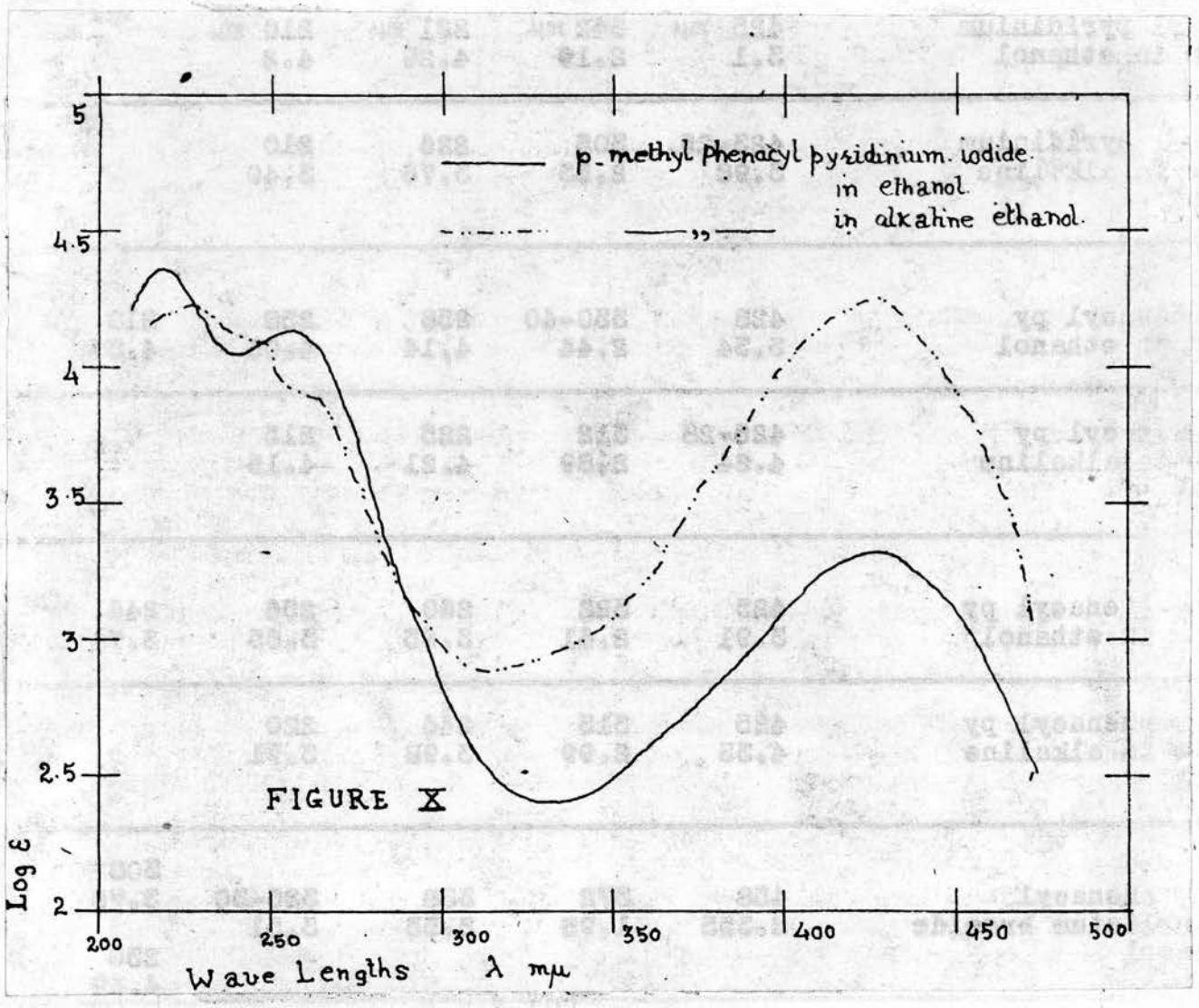

p-methyl phenacyl pyridinium iodide
in ethanol
in alkaline ethanol
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
500
Wave Lengths λ mμ

FIGURE X

The following results were obtained:-

A Table XV.

ound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε
henacyl pyridinium odide in ethanol	425 mμ 3.1	342 mμ 2.19	221 mμ 4.29	210 mμ 4.2	mμ	mμ
henacyl pyridinium odide in alkaline thanol	423-25 3.98	305 2.53	226 3.76	210 3.49		
-me phenacyl py odide in ethanol	428 3.34	330-40 2.44	258 4.14	238 4.05	218 4.37	
-me phenacyl py odide in alkaline thanol	425-28 4.24	312 2.89	225 4.21	215 4.15		
-bromo phenacyl py romide in ethanol	425 3.91	322 2.61	260 3.65	256 3.65	246 3.71	220 3.431
-bromo phenacyl py romide in alkaline thanol	425 4.33	313 2.99	246 3.98	220 3.71		
-bromo phenacyl soquinolinium bromide ethanol	458 2.355	372 1.98	338 3.53	323-30 3.51	308 3.76 230 4.49	302 3.73
-bromo phenacyl soquinolinium bromide in lkaline ethanol	456-58 4.33	343 3.39	Sharp	rise	308 3.96 214 4.61	280-90 3.9

All the phenacyl pyridinium and isoquinolinium halides in neutral solution show an absorption in the region

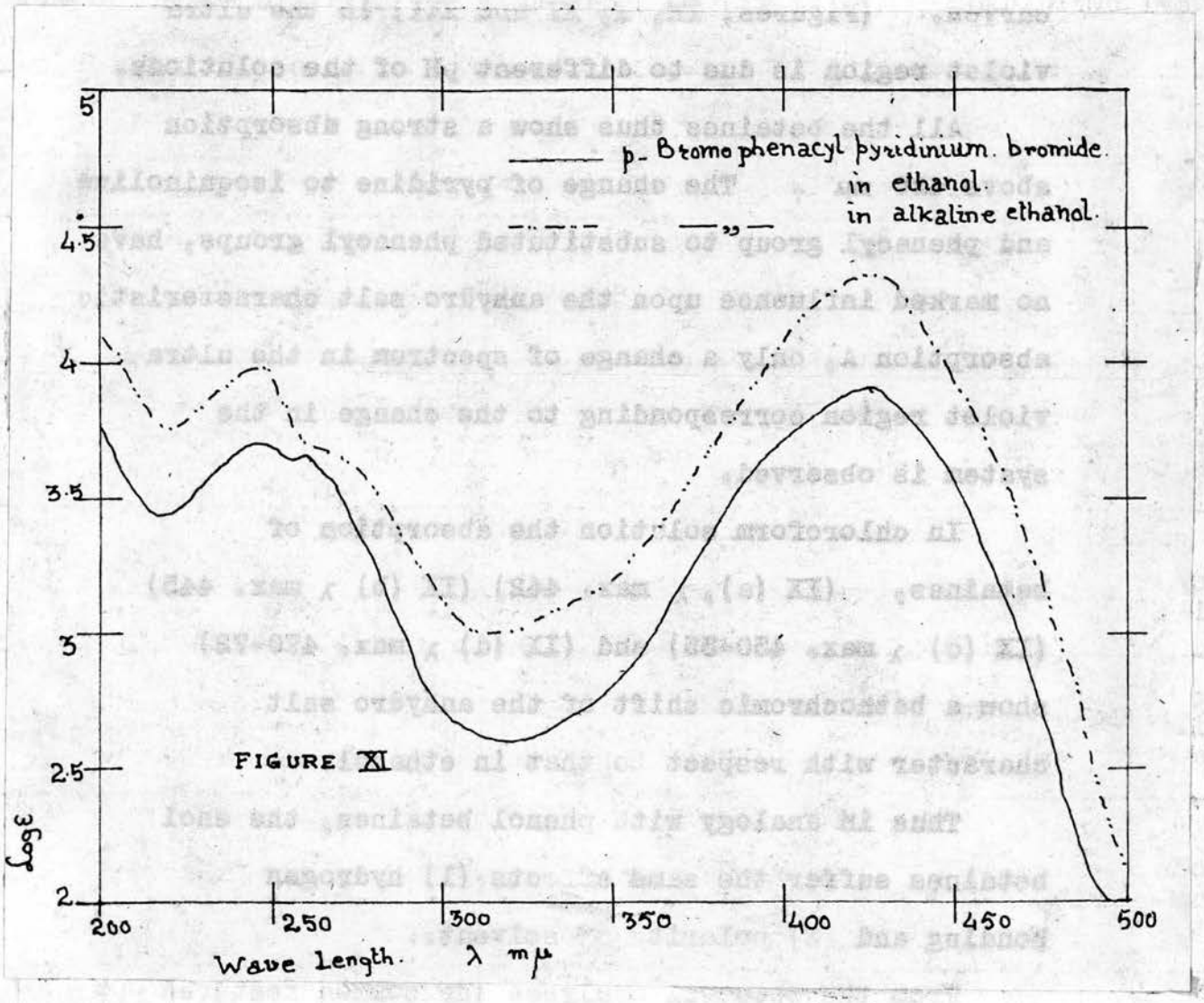

p-Bromophenacyl pyridinium bromide.
in ethanol.
in alkaline ethanol.
5
4.5
4
3.5
3
2.5
2
log ε
200
250
300
350
400
450
500
Wave Length. λ mμ

FIGURE XI

of anhydro salt character A., though the extinction value in that region in comparatively lower than the betaine itself. This absorption is attributed to the partial ionisation of the compounds into the betaine form. The shift in the remaining part of curves. (Figures, IX, X, XI and XII) in the ultra violet region is due to the different pH of the solutions.

All the betaines thus show a strong absorption above 420 mμ . The change of pyridine to isoquinoline, and phenacyl group to substituted phenacyl groups, have no marked influence upon the anhydro salt characteristic absorption A, only a change of spectrum in the ultra violet region corresponding to the change in the system is observed.

In chloroform solution the absorption of betaines, (IX (a), λ max. 442) (IX (b) λ max. 445) (IX (c) λ max. 430-35) and (IX (d) λ max. 470-72) show a bathochromic shift of the anhydro salt character with respect to that in ethanol.

Thus in analogy with the phenol betaines, the enol betaines suffer the same effects (1) hydrogen bonding and (2) polarity of solvent.

From the spectral analyses the common features of $\overline{O}$ betaines could be summed up as, (1) development of a new absorption band, termed as the anhydro salt characteristic band "A", absent in the parent base. This characteristic band is affected by solvents in two ways, (a) a hypsochromic shift due to hydrogen

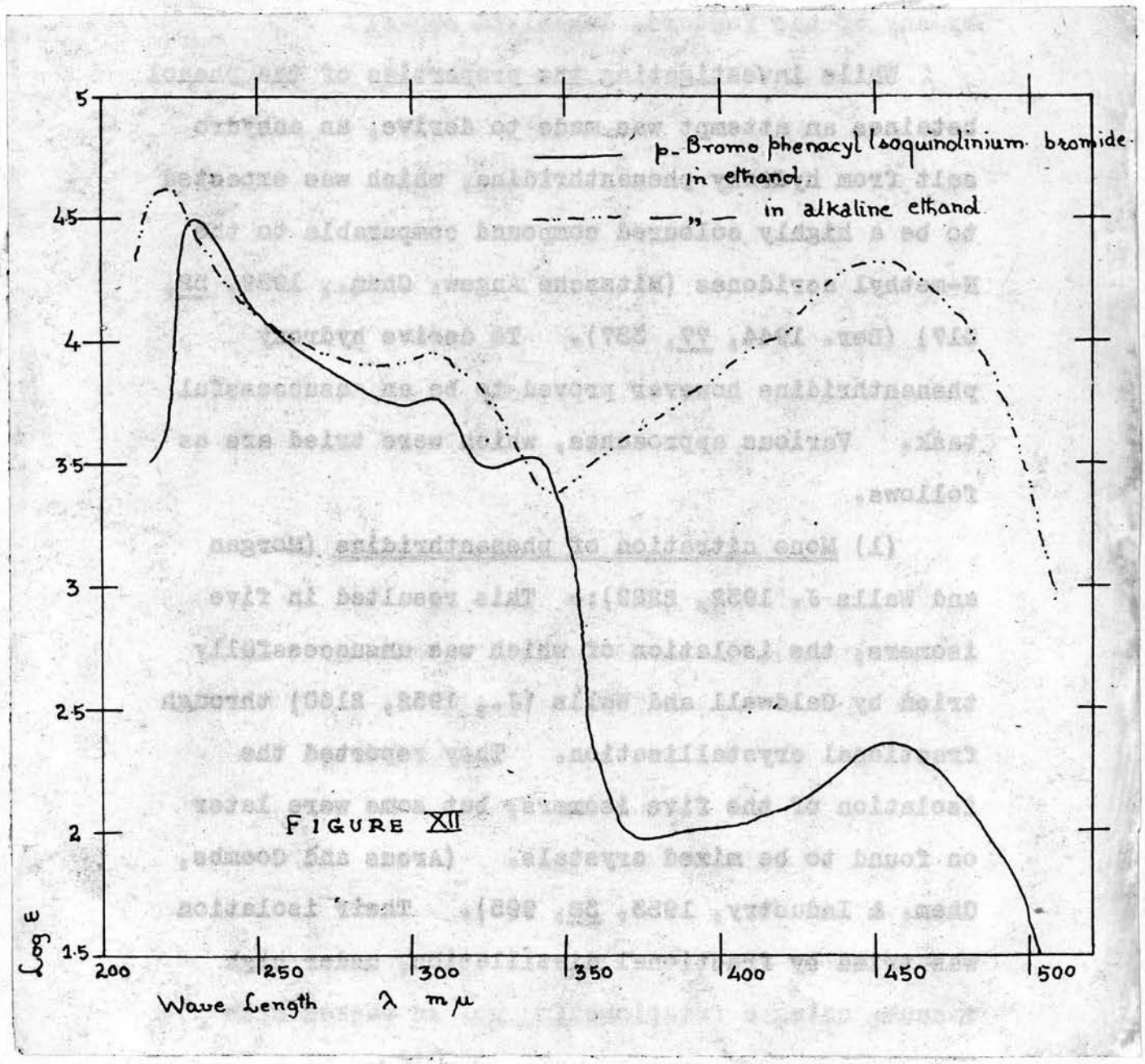

p-Bromo phenacyl isoquinolinium bromide
in ethanol.
" in alkaline ethanol
5
4.5
4
3.5
3
2.5
2
1.5
Log ε
200
250
300
350
400
450
500
Wave Length λ mμ

FIGURE XII

bonding and (b) a bathochromic shift in solvents of decreasing dipole moments, which attains its maximum value in a non polar solvent when the anhydro salt character is fully displayed, uninfluenced by any of the factors, described above.

While investigating the properties of the phenol betaines an attempt was made to derive, an anhydro salt from hydroxy phenanthridine, which was expected to be a highly coloured compound comparable to the N-methyl acridones (Nitzsche Angew. Chem., 1939, 52, 517) (Ber.,1944, 77, 337). To derive hydroxy phenanthridine however proved to be an unsuccessful task. Various approaches, which were tried are as follows.

(1) Mono nitration of phenanthridine (Morgan and Walls,J.,1932, 2229):- This resulted in five isomers, the isolation of which was unsuccessfully tried by Caldwell and Walls (J., 1952, 2160) through fractional crystallisation. They reported the isolation of the five isomers, but some were later on found to be mixed crystals. (Arcus and Coombs, Chem. & Industry, 1953, 38, 995). Their isolation was tried by fractional distillation, under high vacuum, using a fractionating column packed with Dixon rings, but the isomers did not distil well. Chromatography on alumina, using Morin dye to show the bands (nitro-phenanthridines do not fluoresce upon the alumina column under ultra violet light) also

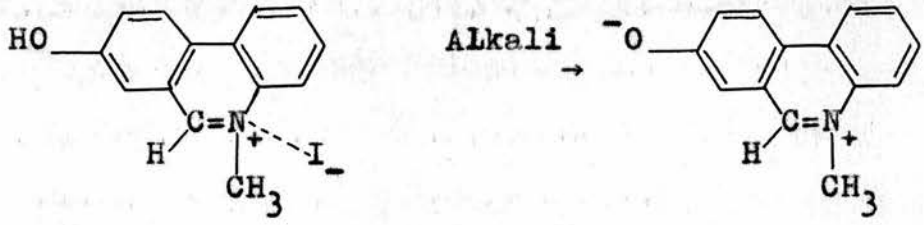
proved abortive.

(2) The starting material this time was fluorene, which was nitrated to 2-nitro fluorene (Diels.,Ber., 1901, 34, 1758) 2-nitrofluorene was oxidised to 2-nitrofluorenone, with sodium dichromate (Diels.,Ber., 1901, 1764). From this, 2-nitro fluorenone oxime, M.P. 263°C. was made. Beckmann's rearrangement of the oxime in a mixture of PCl_5 and BCl_3, yielded a chlorine containing compound M.P. 253-73°C.(yield 90%) (Moore and Huntress, J. Amer. Chem. Soc., 1927, 49, 2622), which on boiling for one hour with glacial acetic acid melted at 280-90°C. Reduction of the so obtained crude 7-nitro phenanthridone with stannous chloride and hydrochloric acid yielded a scarlet crystalline compound in low yield M.P. 160°C. which did not correspond with amino-phenanthridone. Other methods of reduction failed to give any product.

(3) The Schmidt hydrazoic acid reaction (Smith, J. Amer. Chem. Soc., 1948, 70, 323) on 2-nitro fluorenone gave a 90% yield of impure 2-nitrophenanthridone. M.P. 290°C. (on sublimation and recrystallisation from glacial acetic acid). The ketone could not be reduced to phenanthridine by $Li\text{-}AlH_4$ or catalytically. This was therefore converted to thiophenanthridone with P_2S_5, (Taylor and Martin, J. Amer. Chem. Soc., 1952, 74, 6295) which was obtained as orange needles from aqueous pyridine, which decomposed on heating above 250°C. and, gave no fixed

melting point, yield 50%. The thio phenanthridone on treatment with excess of Raney nickel, resulted in a complex mixture of amino and nitro phenanthridine as well as the unchanged starting material, which could not be effectively separated.

(4) An approach is still under consideration through 2-nitro fluorene-9-ol or 2-nitro fluorene-9-azide (Arcus and Coombs, Chem. & Industry, 1953, 995) and subsequent Schmidt Reaction upon them to give the nitro phenanthridine directly. Once nitro phenanthridine is obtained, it could be reduced to amino phenanthridine. And the diazotisation followed by decomposition of diazo compound would result into hydroxy phenanthridine. This compound on quarternisation with methyl iodide, and treatment of the quarternary halide with alkali would yield a highly coloured phenol betaine X, resembling in its properties to other phenol betaines.



X

EXPERIMENTAL

PHENOL BETAINES.

3-hydroxy pyridine compounds:

Preparation of N-methyl 3-hydroxy pyridinium iodide:-

3-Hydroxy pyridine was dissolved in pure analar acetone, and was refluxed with excess of methyl iodide for one hour, when the quarternisation was complete. Excess of acetone and methyl iodide was distilled off, and the remainder was taken up in ethanol. The crystals of the methiodide separated as colourless prisms, on addition of ether to the solution, which melted at 120.5°C. on recrystallisation from alcohol and ether. Analysis calculated ($C_6H_8NOI - H_2O$)

C = 28.23%, H = 3.92%, N = 5.49% I = 49.8%

(found) C = 28.4%, H = 4.01%, N = 5.9%, I = 49.5%

Derivation of the betaine from N-methyl 3-hydroxy pyridinium iodide:-

Treatment of the iodide with aqueous potassium carbonate produced no coloration. The colourless aqueous layer was extracted with chloroform, which was dried over anhydrous potassium carbonate, and then distilled under reduced pressure at low temperature. White crystals of the betaine separated from its concentrated solution of chloroform, on addition of petrol (80-100°C.), which were unstable

and could not be analysed.

Preparation of N-(p-nitrobenzyl) -3-hydroxy pyridinium bromide:-

On refluxing 3-hydroxy pyridine with p-nitrobenzyl bromide in analar acetone for one hour, a high yield of a cream coloured solid was obtained. The solid was filtered and washed with ether to remove excess of p-nitrobenzyl bromide, and unchanged, if any, 3-hydroxy pyridine. The solid was recrystallised from ethanol M.P. 216-17°C., which formed a yellow crystalline picrate M.P. 177°C., analysing 15.3% N. (calculated), 15.8% N. (found); The N-(p-nitrobenzyl)-3-hydroxy pyridinium bromide analysed (2) as Br = 23.8% N = 8.15% (found)

Br = 24.3% N = 8.5% (calculated for $C_{12}H_{11}N_2O_3Br + H_2O$).

Derivation of the betaine:- The straw coloured solution of the bromide was treated with aqueous potassium carbonate in cold, and was then extracted with chloroform. The colourless chloroform layer was dried and distilled as before. From the concentrated chloroform solution the betaine was crystallised by addition of petrol (80-100°C.). This gave the same picrate as the quarternary bromide M.P. 177°C. The betaine was recrystallised from chloroform and benzene, which analysed as (found)

C = 56.1%, H = 4.00%, N = 11.4% ($C_{12}H_{10}N_2O_3 + H_2O$ calculated) C = 56.7%, H = 4.73%, N = 11%

8-hydroxy quinoline compounds:-

Preparation of N-methyl 8-hydroxyquinolinium iodide:-

8-Hydroxyquinoline was refluxed with excess of methyl iodide in analar acetone for 3 hours; separation of yellow crystals occurred. Acetone and methyl iodide were distilled off, and the remainder was washed with ether. The solid was dissolved in ethanol, from which it was recrystallised by the addition of ether M.P. 143°C. (with decomposition).

Analysis N = 5.0%, I = 44.0% (found), N = 4.9%, I = 44.3% (calculated).

Derivation of the betaine:- The treatment of N - methyl : 8-hydroxy quinolinium iodide with 2 N aqueous potassium carbonate in cold gave an orange solution with effervescence, which was repeatedly extracted into chloroform, yielding a violet solution. This was dried over anhydrous potassium carbonate, and then concentrated by distilling under reduced pressure. Orange crystals were obtained from the concentrated solution by the addition of petrol (80-100°C.), which on drying under vacuum over chloroform gave violet red needles. M.P. 115°C. (with decomposition).

The betaine analysed as a monohydrate.

C = 68.4%, H = 6.16%, N = 7.5% (found) and

C = 67.8%, H = 6.2%, N = 7.9% (required for $C_{10}H_9NO - H_2O$)

The same compound has been made by G. Caronna and B. Sansone (Gazz. Chim. Ital.,1939, 69, 24-28) by the action of diazomethane on 8-hydroxyquinoline in etherial solution. The bluish red solid that separated out was found to analyse correctly for the betaine M.P. 115°C. (with decomposition).

C = 75.38%, H = 5.72%, N = 8.96% (found)

C = 75.47%, H = 5.66%, N = 8.80% (calculated)

This compound resembled the betaine, derived by the method described above, which was further confirmed by their identical spectra. The method of drying previous to analysis must be responsible for the observed differences.

Compounds from styryl pyridines:-

The condensation of α-picoline with aromatic aldehydes is well known (M. Chiang and W. Hartung, J. Org. Chem.,1945, 10, 21).

10 gms. of picoline, 13 gms. of salycylaldehyde and 7 gms. of water, were enclosed in a Carius tube which was then maintained at a temperature of 140°C. for 8 hours in an autoclave. The resulting product was transferred to a round bottomed flask, and steam distilled to remove picoline and salycylaldehyde. The oily residue was extracted into ether, and purified with

charcoaled in ethanol. The product was crystallised from petrol (80-100°C.) giving 4.3 gms. of pure pyridyl O-hydroxy phenyl stilbazole. 19.5% M.P. 132°C.

The p-hydroxy phenyl stilbazole was prepared in the same way, using p-hydroxy benzaldehyde instead of salycylaldehyde. The yield was 70% of the theoretical. M.P. 217°C. Meta-hydroxy benzaldehyde, however, failed to give any appreciable yield by the above method, and therefore a different method was pursued.

A mixture of (1 mole) picoline, (0.85 mole) m - hydroxy benzaldehyde and (1 mole) of acetic anhydride, was refluxed on an oil bath at 200°C. for 10 hours. Unchanged picoline was then distilled off at the same temperature and the remainder was poured into cold water. The precipitate obtained was washed with several portions of water and dilute alkali, and then again with water to remove alkali. The solid was purified by charcoaled and recrystallised from ethanol as pale white needles M.P. 136°C. Yield 70%.

Preparation of the methiodides:- All the three compounds gave methiodides readily, by refluxing them with excess of methyl iodide in analar acetone for a period of two hours, when the crystals of the methiodide separated, which were recrystallised from alcohol and ether.

Methiodide of α-pyridyl O-hydroxyl phenyl

stilbazole was obtained as yellow needles. M.P. 240°C. which analysed as

C = 49.04%, H = 3.94%, N = 3.84%, I = 37.0% (found)

C = 49.56%, H = 4.13% N = 4.13%, I = 37.46% (calculated)

Picrate of the methiode was obtained as a yellow crystalline solid analysing N = 13.6% against N = 13.63% (calculated).

Methiodide of α -pyridyl m-hydroxy phenyl stilbazole was obtained as pale yellow needles. M.P. 205-7°C. Analysing C = 49%, H = 4.4%, N = 4.25% I = 37.5% (found), C = 49.56%, H = 4.13%, N = 4.13% I = 37.46% (calculated)

The methiodide of α-pyridyl p-hydroxy phenyl stilbazole crystallises as yellow needles. M.P. 257°C. Analysing

C = 49.5%, H = 4.28%, N = 4.5%, I = 37% (found)

C = 49.56%,H = 4.13%, N = 4.13%,I = 37.46% (calculated)

Derivation of betaines:- (1) The methiodode of O-hydroxy phenyl stilbazole gave an orange coloured betaine on treatment with 2N K_2CO_3 solution in cold. The betaine was quite stable and was extracted into chloroform as purple coloured solution. The chloroform layer was dried over anhydrous Na_2SO_4 and the solution was evaporated at room temperature under reduced pressure. The betaine was crystallised as dark violet needles with chloroform benzene mixture, which

decomposed on melting at 154°C. The analysis shows that betaine crystallises with 2 mols. of water of crystallisation.

C = 67%, H = 6.45%, N = 5.35% (found)

C = 67.9%, H = 6.8%, N = 5.66% (calculated for $C_{14}H_{13}NO + 2H_2O$).

The betaine was readily soluble in water and alcohol in which it gave orange red colour. In chloroform it was less soluble giving violet colour, while in benzene it was least soluble giving a blue coloured solution. The betaine was found to be thermochromic because a blue solution of betaine in chloroform at the temperature of boiling water turned deep blue. While on cooling in Cardice it turned orange red.

Similar treatment of aqueous K_2CO_3, proved unfruitful, with α- pyridyl m-hydroxy phenyl stilbazole methiodide. There was a change in coloration with 2N.- NaOH solution to orange colour which could sparingly be extracted into chloroform. The betaine was very unstable and could not be crystallised.

α- pyridyl p- hydroxy phenyl stilbazole methiodide tends to give orange colour with aqueous K_2CO_3 which was less readily extracted into chloroform as violet solution. The betaine was found to be labile and could not be crystallised.

A short approach to the synthesis of the above

mentioned betaines was undertaken by condensation of α -picoline methiodide (1 mole) with the corresponding hydroxy benzaldehydes (1 mole), in strong alkaline conditions (2 moles of NaOH), in ethanol. The deep orange red coloration developed, which manifested the same properties of the above mentioned betaines in different solvents. But the isolation of pure betaine could not be accomplished on account of their instability to heat and atmospheric oxidation.

Compounds from substituted quinolines:

Preparation of 2- (Ortho-, meta- and para, hydroxy phenyl) quinolines

1 gm. of Ortho amino benzaldehyde, (Bamberger, Ber., 1901, 34, 1330), dissolved in 20 mls. of ethanol, was added to a solution of 1 gm. of the desired hydroxy acetophenone, in 10 mls. of ethanol. This was followed by the addition of another 10 mls. of 10% solution of sodium ethoxide in ethanol. The colour of the solution turned orange red. The solution was warmed slightly over the water bath, and then left over night. The solvent was distilled off, and the solid that was left behind, was suspended in dilute hydrochloric acid, enough to acidify the suspension. This suspension was extracted with ether to remove the unchanged starting material, and was finally neutralised with sodium bicarbonate.

The solid that separated, was filtered and crystallised from the desired solvent.

2- (ortho-hydroxy phenyl) quinoline crystallised as yellow needles from ethanol. Yield 1.2 gms. M.P. 115-17°C. Analysis -

C = 81.29%, H = 4.85%, N = 6.65% (found) and

C = 81.45%, H = 4.97%, N = 6.33% (calculated).

2- (meta-hydroxy phenyl) quinoline crystallised as white needles from aqueous ethanol. Yield 1 gm. M.P. 156-57°C. Analysis:-

C - 81.28%, H - 4.83%, N - 6.38% (found)

C - 81.45%, H - 4.97%, N - 6.33% (calculated).

2- (Para-hydroxy phenyl) quinoline crystallised as white needles from petrol (80-100°C.) and benzene. Yield 1.4 gms. M.P. 237-38°C. Analysis:-

C = 81.53%, H = 5.05%, N = 6.5% (found)

C = 81.35%, H = 4.97%, N = 6.30% (calculated)

<u>Preparation of the methiodides of 2- (O-, m- and p- hydroxy phenyl), quinolines) and subsequent derivation of betaines</u>

2- (Meta-and para-hydroxy phenyl) quinolines readily formed a methiodide by refluxing them with excess of methyl iodide in analar acetone, for two hours, when the quarternisation was complete. But in the case of 2- (O - hydroxy phenyl) quinoline, methanol was used as the solvent, and the period of

reflux with methyl iodide was four hours. After reflux, the solvents were distilled off, and the solid was taken up in ethanol, from which it crystallised out by the addition of ether. Recrystallisation was carried out in the same way, giving excellent yields of the methiodide.

N-methyl-2-(0-hydroxy phenyl) quinolinium iodide. It crystallised from methanol and ether as yellow needles. M.P. 180°C. (with decomposition). The crystals turned black on long keeping due to decomposition. No coloured betaine was isolated on treatment of the methiodide with K_2CO_3 solution. Analysis -

(found) iodine = 34.7%

(calculated) iodine = 34.98%

N-methyl-2- (m-hydroxy phenyl) quinoliniumiodide:- It crystallised from ethanol and ether as yellow needles. M.P. 194-5°C. The methiode on treatment with 2N.K_2CO_3 solution gave an orange coloured betaine which was unstable and could not be crystallised. Analysis -

(found) iodine = 34.85%

(calculated)iodine = 34.98%

N-methyl-2- (p-hydroxy phenyl) quinolinium iodide. It crystallised from ethanol and ether as yellow needles M.P. 209°C. The methiodide on treatment with 2N K_2CO_3 solution gave an orange coloured betaine which was repeatedly extracted with chloroform. This chloroform solution was dried over anhydrous

sodium sulphate which was filtered and then distilled off to a small volume. Some benzene was added in the solution while still hot. Orange needles of the betaine crystallised out on cooling which melted at 85.5°C.

Analysis of the methiodide.

(found) iodine = 34.8%

(calculated) iodine = 34.98%

Analysis of the betaine.

(found) nitrogen = 5.6%

(calculated) nitrogen = 5.96%

ENOL BETAINES

Preparation of phenacyl, and p-methyl phenacyl pyridinium iodide, and the subsequent derivation of the betaines.

The prodedure followed (King, J. Amer. Chem. Soc.,1944, 66, 894) was essentially the same for both compounds. To (0.1 mole) of appropriate ketone viz. acetophenone or p-methyl acetophenone, dissolved in 30-50 mls. of pyridine, (0.1 mole) of iodine was added. The solution was heated for 30 minutes over a steam bath, and let stand over night. The excess of pyridine was filtered off and the mixture of β-ketoalkyl pyridinium iodide and pyridine hydro-iodide was separated by means of their solubility characteristics. In this case,

however, pyridine hydroiodide being more soluble in water, was removed by washing with water, followed by small quantity of ethanol. The product left behind after washing was crystallised from ethanol. Yields recorded in both the cases were 80% and 85% respectively. Phenacyl pyridinium iodide crystallised as white lustrous plates M.P. 215-17°C., and the methyl phenacyl pyridinium iodide was obtained as pale yellow solid M.P. 200-2°C. The melting points were in agreement with those found by King (J. Amer. Chem. Soc., 1948, 70, 239)

Attempts at preparing the betaines in crystalline form from the above quarternary salts by various methods (viz. treatment with dilute potassium carbonate solution in cold, or treatment with silver oxide) proved abortive, despite all precautions of extracting the coloured betaine into chloroform layer, in an atmosphere of nitrogen and in the absence of light, to prevent oxidation. The orange coloured betaines, no sooner they were crystallised from chloroform by the addition of petrol, they started decomposing instantaneously into a green viscous liquid. As such the spectra of betaines were studied by treating the quarternary iodides with solid K_2CO_3 in their alcoholic solutions, in which the betaines were stable. The same procedure was followed in the case of their spectra in chloroform. The freshly generated betaine was extracted

into chloroform, and its spectra was taken immediately.

Preparation of P-bromo phenacyl pyridinium bromide and P-bromo phenacyl isoquinolinium bromide, and the subsequent derivation of the betaines:-

The method of preparation was the same as adopted by Kröhnke (Kröhnke, Ber., 1935, 68, 1177-1193). The betaines evolved failed to analyse correctly, in spite of all the above mentioned precautions, and therefore their spectra too, was studied in the same manner as the previous enol betaines.

Phenol betaine containing two nitrogen atoms contributing to the cationic system:-

6-hydroxy 1'-2'-1-2 pyridobenziminazole (Schmid and Czerney, Monatsh, 1952, 83, 31-5)

21.6 gms. p-quinone. 50 mls. glacial acetic acid	Solution A
9.4 gms. 2 amino pyridine 30 mls. glacial acetic acid	Solution B

Solution A was added to solution B, over a period of 15 minutes. To this 30 mls. of water was added, and the solution was warmed for 5 minutes. 50 mls. of 50% hydrochloric acid was added, and the solution was diluted. It was extracted with ether to remove hydroquinone and quinone. The resulting solution was made alkaline with sodium carbonate, when the

desired compound precipitated. After treatment with charcoal in methanol, the compound crystallised as yellow needles M.P. 285°C. The compound sublimed at 210°C./2 mm. The yield recorded was 6.5 gms.

Preparation of the methiodide:- The usual boiling under reflux, the solution of the compound with excess of methyl iodide in analar acetone, resulted in a pale yellow powder which was soluble in water, and did not contain requisite amount of iodine.

The compound was, therefore dissolved in methanol and boiled under reflux, with excess of methyl iodide for three hours. The solvent and excess of methyl iodide were distilled off, and the residual solid was crystallised from ethanol as white needles, M.P. 302°C. (with decomposition), analysing for a monohydrate.

Analysis

C = 36.3%, H = 3.47%, N = 8.1%, I = 36.3%, (found)

C = 36.9%, H = 3.7%, N = 8.1%, I = 36.9%, (calculated for the methiodide + H_2O).

p-nitro benzyl bromide derivative was prepared in an identical way as the methiodide. The solid left after quarternisation, was washed with ether to remove excess of p-nitro benzyl bromide. The residue was crystallised from ethanol as white needles.

M.P. 298°C.

Analysis

C = 54%, H = 3.4%, N = 10.7%, Br = 20% (found)

C = 54%, H = 3.5%, N = 10.5%, Br = 20% (calculated)

Derivation of the betaine from the methiodide:- Usual treatment of the methiodide with aqueous sodium carbonate, resulted in a yellow colour which could not be extracted into chloroform. Sodium hydroxide solution also failed to produce any result.

The betaine this time was liberated by the action of silver carbonate on the methiodide in ethanol. The solution of methiodide was warmed with slight excess of silver carbonate, and then filtered. The solution was concentrated to a small volume, and then the betaine was crystallised from 50% alcohol benzene mixture giving orange needles. The betaine was readily soluble in water and alcohol, less soluble in chloroform and insoluble in benzene. It readily takes up moisture and tends to crystallise with molecules of water or alcohol of crystallisation which could not be removed even on drying at the temperature of boiling water under reduced pressure (as shown by the analysis). At temperaturesabove 150°C. the betaine decomposed turning red and then brown, and had no fixed melting point. In water and alcohol it gave a yellow coloured solution, in chloroform it was orange yellow and in benzene (in which

it was dissolved by dissolving it first in small quantity of alcohol and then suspending it in large volume of benzene, then distilling off alcohol as azeotrope) it gave a pink coloured solution while hot and then it became colourless when the crystals separated out on cooling.

Action of excess of dry diazomethane in ether over the suspended 6-hydroxy 1'-2'-1-2 benziminazole in ether, gave yellow crystals which showed the same properties as the betaine.

Analysis:- The betaine dried in vacuum at the temperature of boiling chloroform:-

C = 64.3%, H = 6.2%, N = 11.9% (found)

C = 61.3%, H = 6.3%, N = 11.9% (betaine + 2 H_2O calculated).

The betaine dried in vacuum at the temperature of boiling water.

C = 70%, H = 5.01%, N = 13.4% (found)

C = 72.7%, H = 5.05%, N = 14.1% (calculated)

(The anomaly in the analysis is due to the presence of solvent of crystallisation).

SECTION (B)

Section (B)

The $\overline{C}$ betaines (YLIDES):-

The object was to prepare stable ylides from quarternary ammonium halides, and study their absorption spectra in the visible and ultra violet region, in solvents with differing polar properties, with a view to correlate them with their anhydro salt structure, in anology with $\overline{O}$-betaines.

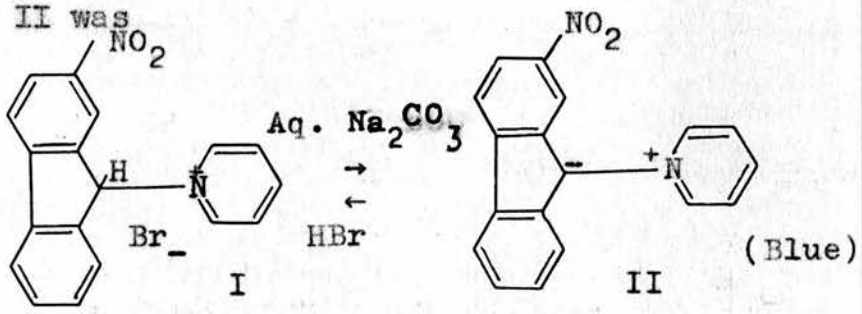
Fluorenylides (Krollpfeiffer and Schneider, Annalen, 1937, 530, 34) were chosen for intensive investigations, which were derived from the quarternary ammonium bromides. These were made by coupling 9-bromo fluorene, 2-nitro-9-bromo-fluorene, and 2:7-dinitro-9-bromo fluorene with pyridine, α-picoline, quinoline and isoquinoline.

The stability of the ylides and hence the chance of obtaining them in pure solid state, was expected to increase with the order given (see introduction) due to deactivating influence of the nitro group.

The starting materials were, fluorene and the above mentioned heterocyclic bases. Fluorene, 2-nitro fluorene (Diels., Ber., 1901, 34, 1758), 2:7-dinitro fluorene (Morgan and Thomason, J., 1926, 269) were subjected to bromination in the 9 position with N-bromosuccinimide. 2:7-dinitro fluorene gave no bromination product. Pyridine and isoquinoline successfully coupled with 9-bromo fluorene and 2-nitro

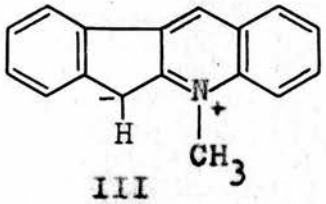
-9-bromo fluorene, but neither α-picoline nor quinoline formed a quarternary ammonium bromide, in which case probably the coupling was sterically hindered.

The general procedure for the ylide formation was to shake the quarternary ammonium fluorenyl bromide (e.g. I) with dilute sodium carbonate solution, and extract the deep colour developed into chloroform layer. The ylide II was

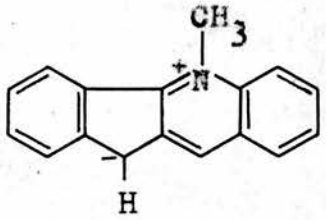


precipitated out of the concentrated chloroform solution by the addition of a large excess of petrol ether. The ylides proved elusive and only 2-nitro-9-pyridinium and isoquinolium fluorenylides could be isolated in solid state, which failed to analyse (probably due to contamination with decomposition product as well as solvent of crystallisation). Although a trace of the greenish black powder of the former or the brown black powder of the latter gave a bright blue colour in chloroform, which faded to yellow colour on standing. The decomposition of ylides could be prevented by using oxygen free pure spectroscopic chloroform, obtained by bubbling nitrogen through pure boiling chloroform. A freshly prepared solution in such pure chloroform was used

for spectroscopic examination, as soon as it was made, which roughly obeyed the Beer's law. For comparative purposes indeno quinolines were synthesised (Cf. Armit and Robinson, J. 1922, 837) and the ylides derived from their quarternary iodides (see experimental) were studied. These ylides, III and IV, also proved difficult to isolate due to their extreme instability. Their absorption spectra



III



IV

were studied from their freshly prepared solutions in pure chloroform, as soon as they were made. The solutions roughly obeyed the Beer's law.

Table I gives the wavelengths of maximum and minimum absorption, by a freshly prepared solution of the ylide in oxygen free spectroscopic chloroform.

Table I

A

Compound	λ max. λ min.	λ max. λ min.	λ max. λ min.	λ max. λ min.	λ max. λ min.
-pyridinium fluorenylide	625 Mμ 598 mμ	395-400mμ 365 mμ	325 mμ 315 mμ	258 mμ 238 mμ	235 mμ mμ
-nitro "	625-30 592	Sharp rise	325 318	290-88 264	245
-isoquinolinium "	675 556	390-95 inf.	Sharp rise	258	
-nitro " "	675 576	Sharp rise	323-25 320	290-88 262	240
-me 2:3-(2':3'-indeno) uinolinium hydroxide nhydro salt	645 600 inf.	335 290-95	263 235-40		
-me 2:3-(3':2'-indeno) uinolinium hydroxide nhydro salt	530 377	285 248-50	235		

All the ylides show a strong absorption of light above 500mμ, the so termed anhydro salt characteristic band "A". Such an absorption in the higher wavelengths is associated with the $\overline{C}$ ionic.structure of the ylides. The absorption of the fluorenylides in the ultra violet region, show great resemblance to the absorption of fluorene or 2-nitro fluorene, which ever residue is present in the ylide. Slight deviations in absorption are due to the contribution of the base (pyridine or isoquinoline) to the total absorption.

The indenoquinolinium anhydro salts apart from the characteristic anhydro salt absorption "A" in the visible region, resemble in their absorption in the ultra violet region, the corresponding indenoquinolines from which they are derived.

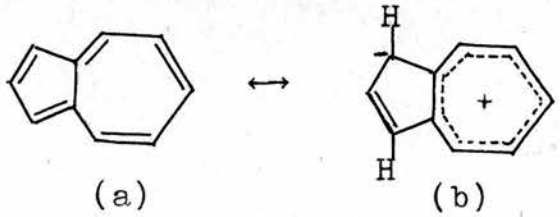
To study the effect of the solvents of differing polarity, on the ylides, the stable, 2-nitro-pyridinium fluorenylide was selected, and the position of maximum absorption in the visible region (the anhydro salt character "A") by the ylide, in different solvents were found. Table II gives the wavelengths of maximum absorption in different solvents.

Table II

Solvent (pure)	Dipole Moment	λ max.
Acetonitrile	3.6	590 mμ
Acetone	2.7	600
Chloroform	2	625
Benzene	polarisable	625
Carbontetra chloride	zero	625

A bathochromic shift of the anhydro salt absorption character "A" of the ylide, in solvents of decreasing polarity is observed, in analogy with the $\overline{O}$-betaines, which is significant of the alignment of the dipolar solute and solvent molecules.

In ethanol there is a shift to 620 mμ probably due to the Dipole interaction. Hydrogen bonding seems impossible and it would appear that in comparison with chloroform the absolute value of the dipole-moment is not involved but the efficiency with which orientation or association of the dipolar structures can occur. In comparison with other solvents decomposition in alcohol is much more rapid and this value for maximum, possibly may not be exact. However the fundamental dependence on solvent polarity is a common feature to the ylide and $\overline{C}$-betaines as in the $\overline{O}$-betaines. Structurally ylides have been put on par with the azulenes (W.H. Stafford and D.H. Reid, Chem. & Industry, 1954, 277-78). The deep blue colour of the ylides, their high dipole-moments, effect of solvents of differing polarity on their spectra, are comparable to those of azulenes. Thus azulenes are deep blue in colour having significant dipole-moments. They show a hypsochromic shift in their characteristic absorption with the increasing dipolar interaction of the solvent. Azulene is therefore reasonably represented as a hybrid [V (a) and (b)] of the classical purely covalent form together with the betaine structure in which the carbanionic portion is analogous to that of II, III and IV.

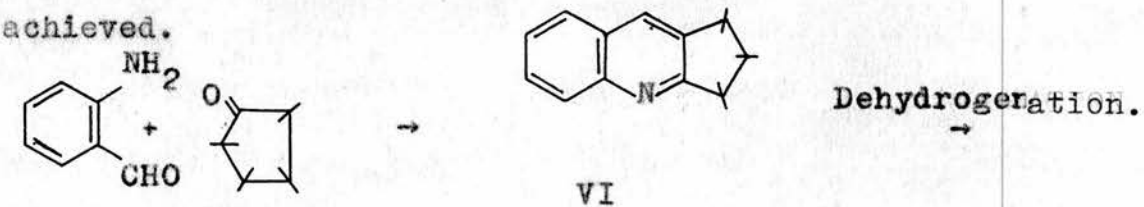


(a) (b)

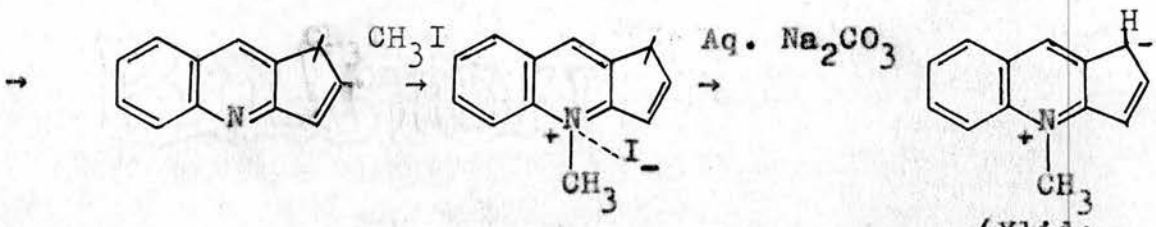
V

and the cationic function is fulfilled by the cyclo-heptatrienylium ion, equivalent to the quarternary nitrogen cation in the ylide.

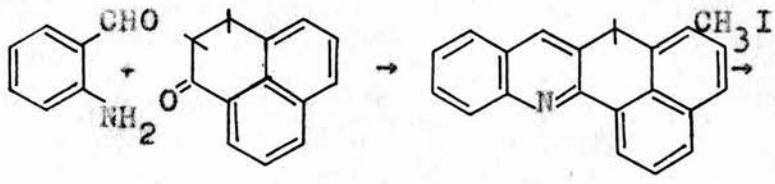
Attempts were made to synthesise an ylide from 2:3-cyclo-pentino quinoline through its methiodide, equivalent to benzazulene. But dehydrogenation of 2:3-cyclopentano quinoline VI (which was obtained as condensation product from cyclopentanone and O-amino-benzaldehyde) to 2:3-cyclo-pentino quinoline could not be achieved.



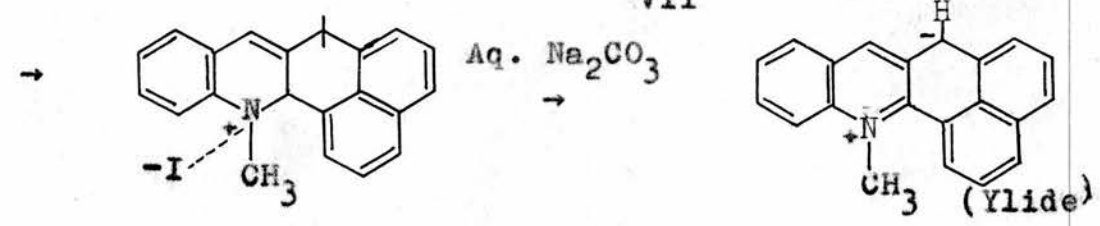
VI

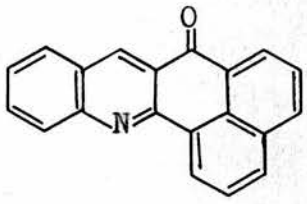


Another condensation of O-amino-benzaldehyde with perinaphthindanone gave salmon pink needles from ethanol M.P. 234°C. correctly analysing for the compound VII.



VII



VII —Oxidation CrO_3→ 

VIII

Analysis:-

C = 89.5%, H = 5.0% N = 5.3% (found)

C = 90%, H = 4.9%, N = 5.2% (calculated).

The compound gave a red coloured crystalline methiodide, M.P. 226°C., by the usual methods; but failed to give a coloured ylide on treatment with alkali. The methiodide on treatment with silver oxide in alcohol gave the compound VII (confirmed by mixed melting point and analysis). The compound VII on oxidation with chromic acid in glacial acetic acid at 100°C. yielded a yellow crystalline solid M.P. 217-18°C. Analysing for the ketone VIII.

C = 85.0%, H = 4.2%, N = 4.5% (found)

C = 85.4%, H = 3.9%, N = 4.9% (Calculated)

Decomposition of 2-nitro-9-pyridinium fluorenylide in dilute chloroform solution:-

To investigate the decomposition and the subsequent unstability of the ylides, the decomposition of 2-nitro -9-pyridinium fluorenylide was closely studied.

Bright blue chloroform solution of this ylide rapidly decomposed to give yellow solution. The decomposition occurred at room temperature, in the atmosphere and in presence of daylight. The decomposition could be retarded by the following factors.

(a) Placing the solution in dark, in an atmosphere of nitrogen.

(b) Excluding oxygen from the solution.

(c) Adding a few crystals of hydroquinone.

The decomposition was accelerated by the following factors

(a) Bubbling oxygen through the solution in daylight.

(b) Ultra violet irradiation.

(c) Addition of small amounts of dibenzoyl peroxide.

The decomposition products on examination were found to be 2-nitro-fluorenone which was obtained in good yield, and pyridine was detected by its odour. Formation of 2-nitro-fluorenone shows that the decomposition is mainly due to oxidation of the carbonanion.

To study the order of the reaction taking place during decomposition through various factors mentioned

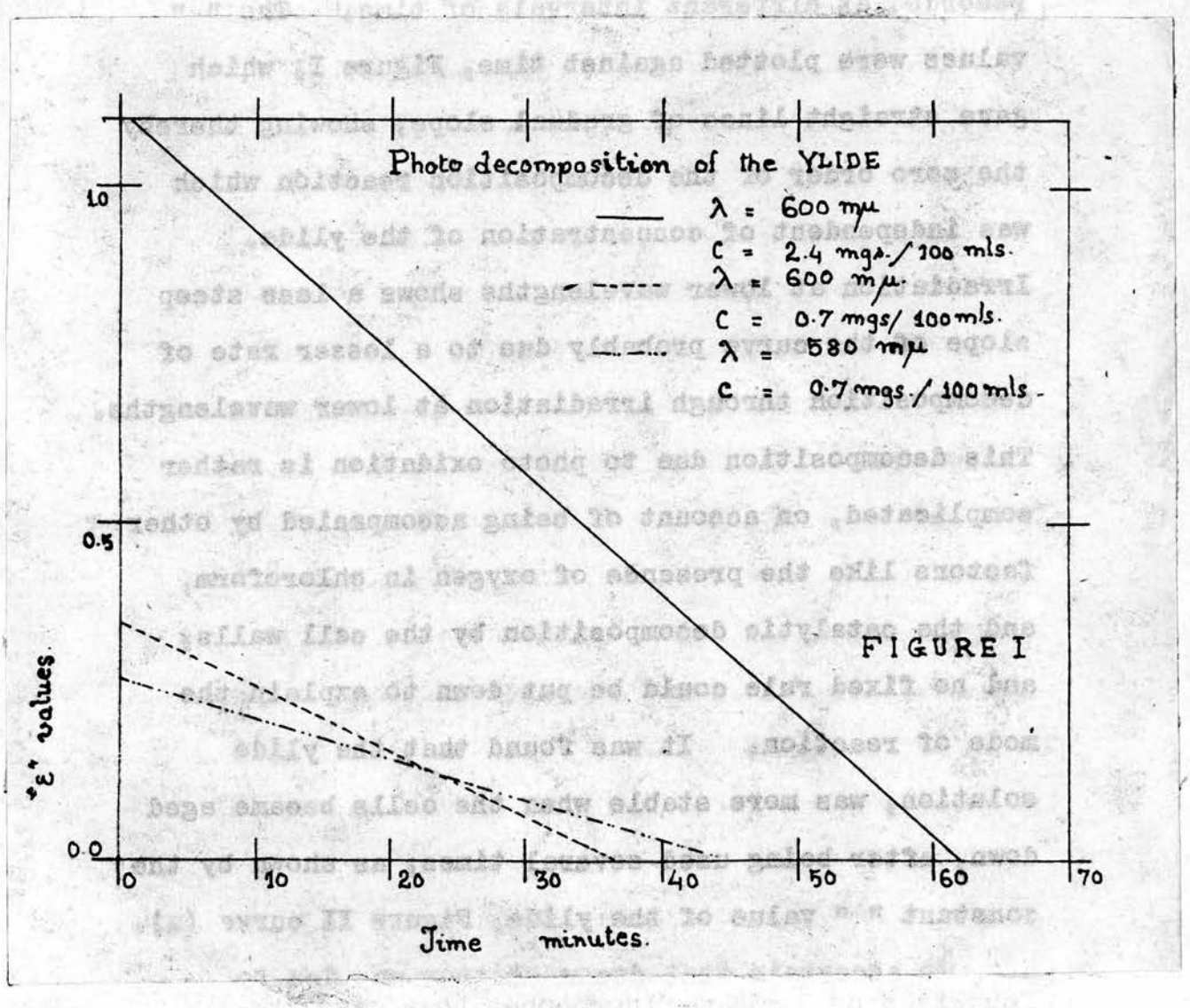


Photo decomposition of the YLIDE
λ = 600 mμ
C = 2.4 mgs./100 mls.
λ = 600 mμ.
C = 0.7 mgs/100 mls.
λ = 580 mμ
C = 0.7 mgs./100 mls.
1.0
0.5
0.0
'ε' values
0
10
20
30
40
50
60
70
Time minutes.

FIGURE I

above the following experiments were carried out.

(i) The decomposition of the ylide in chloroform solution at different concentrations was followed by the Unicam Spectrometer. The ylide solution (of concentration C) was irradiated with a fixed wavelength of light $\lambda m\mu$, and the value of the absorption "ε" was recorded at different intervals of time. The "ε" values were plotted against time, Figure I, which gave straight lines of gradual slope, showing thereby the zero order of the decomposition reaction which was independent of concentration of the ylide. Irradiation at lower wavelengths shows a less steep slope of the curve probably due to a lesser rate of decomposition through irradiation at lower wavelengths. This decomposition due to photo oxidation is rather complicated, on account of being accompanied by other factors like the presence of oxygen in chloroform, and the catalytic decomposition by the cell walls, and no fixed rule could be put down to explain the mode of reaction. It was found that the ylide solution, was more stable when the cells became aged down, after being used several times, as shown by the constant "ε" value of the ylide, Figure II curve (a).

To ascertain that decomposition was due to oxidation, catalytic oxidation with dibenzoyl peroxide was studied. Addition of dibenzoyl peroxide immediately brought about the decomposition of the

ylide, shown by the sharp fall of the curve after 10th minute when the dibenzoyl peroxide was added. Figure II curve (a).

Addition of dibenzoyl peroxide in (1) ordinary and (2) oxygen free solution of the ylide in chloroform yielded the curved (b) and (c) Figure II. The slope of the former curve was sharper than the latter, showing thereby that oxygen in the solvent is also responsible for decomposition.

The catalytic decomposition of the ylide is checked by the addition of a drop of saturated solution of hydroquinone. This gave the curve (d) Figure II which shows a gentle fall of absorption values ending into a steady absorption shown by the straight line of the curve.

Thus the decomposition reaction of the ylides is very complicated and possibly occurs by more than one mechanism.

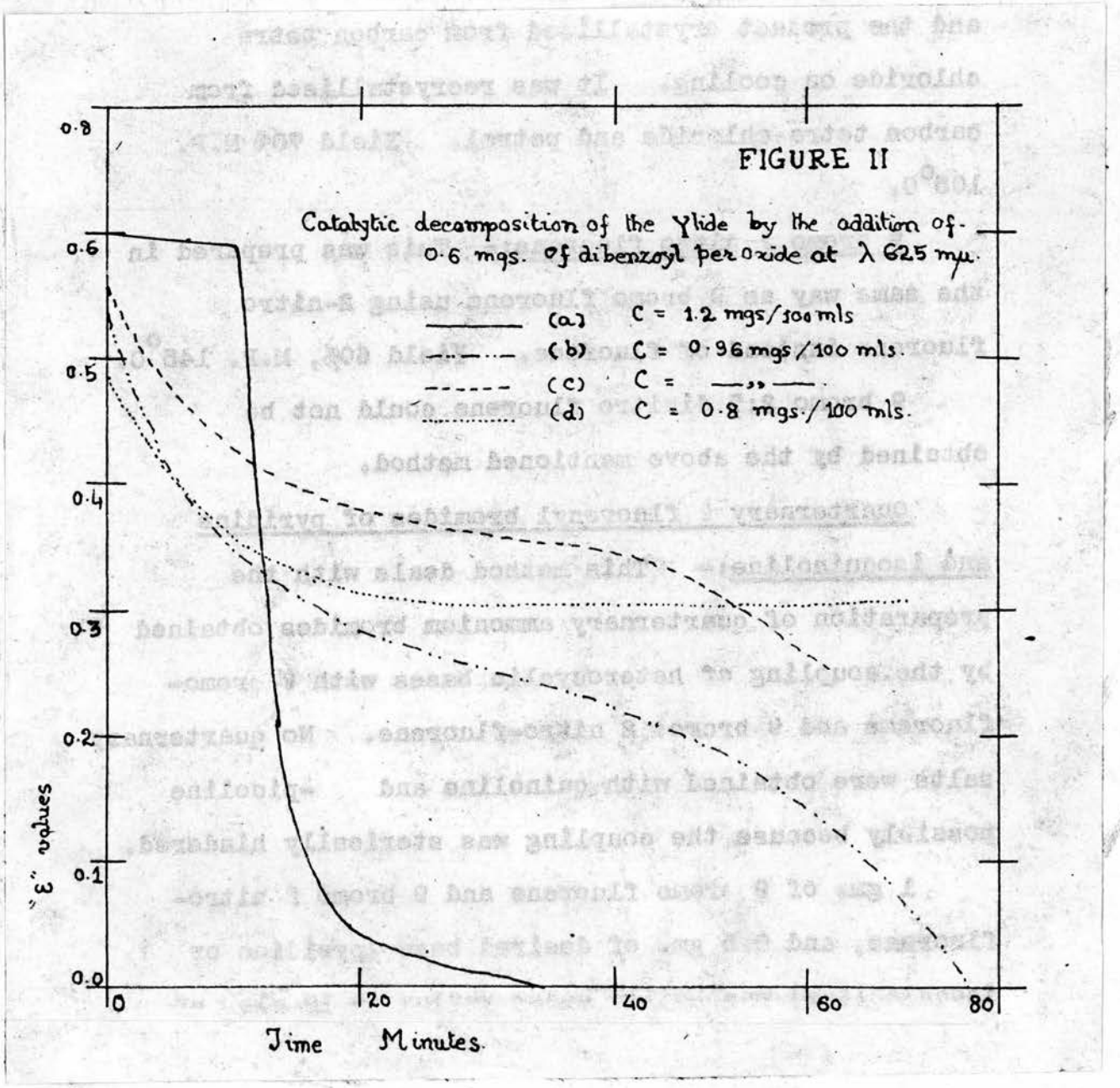


FIGURE II
Catalytic decomposition of the Ylide by the addition of 0·6 mgs. of dibenzoyl peroxide at λ 625 mμ.
(a) C = 1·2 mgs/100 mls
(b) C = 0·96 mgs/100 mls.
(c) C = —,,—.
(d) C = 0·8 mgs./100 mls.
"ε" values
0·8
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0
20
40
60
80
Time Minutes.

EXPERIMENTAL

9-Bromofluorene:- 12 gms. of fluorene was boiled under reflux for seven hours, with 1.2 moles of N-bromsuccinimide in 180 mls. of dry carbon tetra chloride as solvent. The solution was filtered hot and the product crystallised from carbon tetra chloride on cooling. It was recrystallised from carbon tetra chloride and petrol. Yield 70% M.P. 105°C.

9-bromo-2-nitro fluorene:- This was prepared in the same way as 9-bromo fluorene using 2-nitro fluorene instead of fluorene. Yield 60%, M.P. 145°C.

9-bromo 2:7-dinitro fluorene could not be obtained by the above mentioned method.

Quarternary 9-fluorenyl bromides of pyridine and isoquinoline:- This method deals with the preparation of quarternary ammonium bromides obtained by the coupling of heterocyclic bases with 9-bromo-fluorene and 9-bromo: 2-nitro-fluorene. No quarternary salts were obtained with quinoline and α-picoline possibly because the coupling was sterically hindered.

1 gm. of 9-bromo fluorene or 9-bromo 2-nitro-fluorene, and 0.5 gm. of desired base (pyridine or isoquinoline) was boiled under reflux in 10 mls. of analar acetone, for 1 hour. A white solid separated which was filtered after cooling and washed with excess of ether, to remove the unchanged starting material. The solid was crystallised from alcohol

and ether. While using 9-bromo fluorene as the coupling reagent, a bright red solid was deposited along with the quarternary halide. This was presumably due to the formation of bis-biphenylene ethylene, the proportion of which increased with the time of reflux.

Fluorenyl 9-pyridinium bromide:- It was obtained as crystalline white needles M.P. 192°C. Yield 30%.

Fluorenyl 9-isoquinolinium bromide:- White needles were obtained after 2 hours of reflux. M.P. 240-42°C. Yield 50%. Picrate M.P. 180°C.

2-nitro-fluorenyl 9-pyridinium bromide:- A white crystalline solid separated after three hours of reflux. M.P. 126-28°C. It forms a crystalline picrate M.P. 228°C.

Analysis of the bromide

N = 7.6%	Br = 21.1%	(found)
N = 7.6%	Br = 21.6%	(calculated).

2-nitro-fluorenyl 9-isoquinolinium bromide:- It was obtained as white crystalline solid after a period of three hours of reflux. Yield 30%. M.P. 230°C. Picrate M.P. 200°C. (with decomposition).

Analysis:-

N = 5.82%	Br = 16.65%	(found)
N = 6.68%	Br = 19.06%	(calculated)

(Note $\frac{Br}{N}$ ratio = 2.86% (found) and 2.85% (calculated) The difference in analysis is due to hydration.

Derivation of the "ylide" (the anhydro salt) from the quarternary fluorenyl bromide:- 0.5 gms. of quarternary fluorenyl bromide was dissolved in 15 mls. of hot water, and filtered to remove the red insoluble material (probably bisbphenylene ethylene). The cold aqueous solution was placed in a separating funnel, with about 50 mls. of chloroform. 20% sodium carbonate solution was added dropwise, and the purple colour that formed was extracted into chloroform by shaking, giving a deep blue solution of the ylide. The aqueous layer was extracted with another 20 mls. of chloroform. A slight excess of sodium carbonate was present, and the third extraction did not give any appreciable colour in the chloroform layer. The chloroform layer was dried over anhydrous potassium carbonate, and then concentrated in vacuum, at low temperature. Petrol ether (40-60^{o}C.) was added to the concentrated solution to crystallise out the ylide.

9-pyridinium fluorenylide anhydro salt:- The isolation of the crystalline ylide was impossible due to its extreme instability. The absorption spectrum of the ylide was taken, as soon as it was extracted into oxygen free chloroform layer (made by bubbling nitrogen through spectroscopic chloroform). Such a solution roughly obeyed the Beer's law. The decomposition of the ylide sets in as soon as it is generated, through photo oxidation and

atmospheric oxidation.

9-isoquinolinium fluorenylide anhydro salt:- Like the previous ylide, this substance as well, proved elusive, and its spectral analysis was made in the same way as 9-pyridinium fluorenylide.

2-nitro-9-pyridinium fluorenylide anhydro salt:- This was obtained as a black or green powder, which was not crystalline in its appearance under the microscope. The powder was dried in vacuum over P_2O_5. Small quantity of it in chloroform gave a bright blue colour. It gave the same picrate as the quarternary bromide M.P. 226-30°C. (with decomposition.) On heating it decomposes to a grey powder at 200°C. which did not give colour in chloroform. Yield of the ylide was 80%. The ylide decomposes in alcohol. A recrystallisation of the ylide from hot chloroform resulted in the same black green powder, which was used for the spectroscopic measurements. The solution of ylide in oxygen free chloroform roughly obeyed Beer's law.

2-nitro-9-isoquinolinium fluorenylide anhydro salt:- In this case the ylide was too unstable to precipitate as above. The isolation was accomplished by using oxygen free pure spectroscopic chloroform. The chloroform layer after drying over anhydrous potassium carbonate, and then concentrating, gave a good yield of a brownish black powder with petrol

ether. This was dried in vacuum over P_2O_5 and then used for spectroscopic examination. The solution of the ylide in pure chloroform roughly obeyed the Beer's law. The ylide decomposed into a grey powder on heating at 150-60°C., which did not give any colour in chloroform. It gave a picrate, M.P. 200°C. (with decomposition), same as the one from the quarternary bromide.

The powder did not analyse for the pure ylide due to its instability and susceptibility for hydration.

N = 7.5%, H = 4.2%, C = 76.5% (found)

N = 8.8%, H = 4.3% C = 81.5% (calculated)

N-methyl 2:3-(2':3' indeno) quinolinium iodide:-

1 gm. of β-keto-hydrindone (Levin, Graham and Kolloff, J. Org. Chem., 1944, 9, 380) and 1 gm. of O-aminobenzaldehyde (Bamberger, Ber., 1901, 34, 1330) were dissolved in 20 mls. of ethanol, 10 mls. of 20% sodium ethoxide solution in ethanol were added in cold. The colour of the solution changed to orange red. The solution was warmed for 15 minutes and let stand overnight. Ethanol was distilled off and the residual solid was taken in benzene and chromatographed on alumina. A yellow band separated on elution with benzene, which on distillation left a yellow solid (indeno quinoline). The solid was dissolved in analar acetone and boiled under reflux for 2 hours, with excess of methyl iodide. Deep

purple crystals of the methiodide separated, which were filtered on cooling and washed with acetone and ether. Yield 500 mgs. M.P. 204-5°C.

Analysis:

C = 56.8%, H = 4.4%, N = 4.0%, I = 35.3% (found)

C = 56.8%, H = 3.9%, N = 3.9%, I = 35.4% (calculated)

Derivation of the ylide, N-methy 2:3-(2':3'-indeno) quinolinium hydroxide anhydro salt:- The procedure adopted was the same as for the fluorenylides. The ylide gave purple coloured solution in chloroform, from which it was crystallised, but it was found to be very unstable and could not be analysed. The spectrum was consequently analysed from a freshly prepared oxygen free chloroform solution of the ylide which roughly obeyed the Beer's law.

N-methyl 2:3-(3':2'-indeno) quinolinium iodide

The pattern of the preparation followed was the same as the previously described indeno quinoline. α -keto hydrindone (Ingold and Piggott, J., 1923, 123, 1483) was condensed this time with O-amino benzaldehyde, yielding 2:3-(3':2'-indeno) quinoline as white needles. M.P. 152°C. Yield 800 mgs.

Analysis

C = 88.6%, H = 5.2%, N = 5.7%, (found)

C = 88.5%, H = 5.1%, N = 6.4% (calculated)

The indeno quinoline on quarternisation with methyl

iodide in the usual way, yielded a pale yellow crystalline methiodide. M.P. 223°C.

Analysis

C = 56.6%, H = 4.0%, N = 3.8%, I = 34.6% (found)

C = 56.8%, H = 3.9%, N = 3.9%, I = 35.4% (calculated).

Derivation of the ylide, N-methyl 2:3-(3':2'-indeno) quinolinium hydroxide anhydro salt:- Treatment of the methiodide with aqueous potassium carbonate, yielded a pale blue colour in chloroform. The ylide had a fleeting existence and the colour in chloroform, on keeping, soon changed into pale yellow. The spectrum of this anhydro salt was taken in the same way as described before. Its solution in pure chloroform roughly obeyed the Beer's law.

Photo-oxidation of ylide:- 80 mgs. of 2-nitro-9-pyridinium fluorenylide in 80 mls. of chloroform was irradiated for two hours, with ultra violet light, while a rapid stream of oxygen was passed through the solution. The dark red solution thus obtained, was evaporated, and the residue was taken up in benzene. The benzene solution was chromatographed on an alumina column, and on elution with benzene two bands moved down the column. The faster moving band contained a negligible amount of pale yellow solid. The second bright yellow band was eluted, and on distillation of the solvent, yielded yellow solid. This was recrystallised from ethanol.

M.P. 219°C., Yield 70%. Mixed melting point of this substance with 2-nitro fluorenone was undepressed. The yellow product yielded a phenyl hydrazone. M.P. 209-12°C. (with decomposition).

Analysis of phenyl hydrazone

C = 69.2%, H = 3.2%, N = 6.0% (found)

C = 69.3%, H = 3.1%, N = 6.2% (calculated for phenyl hydrazone of fluorenone).

The third band that separated on using traces of ethanol with benzene, for elution, yielded a non crystalline residue which smelt of pyridine.

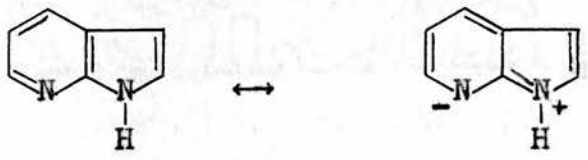
Atmospheric decomposition of ylide:- 1.25 gms. of the ylide in 250 mls. of chloroform was let stand for 4-5 days in an unstoppered flask. The red solution that was obtained, was concentrated to a small volume, and chromatographed on alumina, using chloroform as the eluent. The first band that separated, contained 2-nitro fluorenone (confirmed through its mixed melting point) Yield 60%. The second band that separated contained a non-crystalline product which smelt of pyridine.

SECTION (C)

Section C

The N-Betaines:- The absorption spectra of anhydro salt derivatives of 7-azaindole, 2-pyridylindoles and the carbolines, are described and discussed, to determine the influence of betaine structure, on the spectral properties of the substances.

Derivatives of 7-azaindole:- 7-azaindole, I, (Kruber, Ber., 1943, 76, 130; Clemo and Swan, J., 1945, 604), possesses a nitrogen atom capable of donating electrons (the pyrrole nitrogen atom) and one capable of accepting electrons (the pyridine nitrogen atom). This opposition of tendencies within a resonating system could lead to large betaine type structure, I (b), together with the expected covalent type I (a).



(a) I (b)

Such contribution would be expected to cause a difference in the absorption spectrum of 7-azaindole compared with that of indole.. In addition, the acidic and basic character would both be enhanced. The absorption spectrum is however very similar to that of indole, and the small changes which occur on the addition of acid or sodium ethoxide, to the ethanol in which the spectrum is determined indicate

that contributions of type I (b), must only be minor ones.

Table I gives a comparative study of the absorption spectra of indole and 7-azaindole.

Table I.

Compound	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε
Indole	265) 3.84 280) 3.73 287) 3.62	237 3.28	219 4.42
7-azaindole in ethanol	290 3.86	239 2.73	218-19 4.31
7-azaindole in ethanol + Hcl.	292 3.89	243 2.29	223 4.23
7-azaindole in ethanol + NaO.Et.	290 3.86	240 2.70	222 4.14

The only marked difference in the absorption of the two compounds lies in the position of the maximum, in the longest wavelengths; but even this is what would be expected on the analogy of naphthalene compared with quinoline or isoquinoline. In this case the long wave absorption band is broadened by introducing a hetero atom, and if the finer structure is ignored the mean of the band is effectively shifted bathochromically.

7-azaindole readily forms quarternary derivatives

and these on treatment with alkali, yield yellow basic substances which can be extracted into chloroform. The products on the whole analysed well, for the expected anhydro salts, although in the case of methyl derivative some difficulty was experienced, due apparently to a tendency to take up water. These anhydro salts are capable of formulation as normal covalent compounds and also as betaines, II (a) and (b).

(a) ↔ (b)

II

(α)R = CH_3
(β)R = $CH_2.C_6H_5$
(γ)R = $CH_2.C_6H_4.NO_2(-p)$

The absorption spectra of these compounds were examined, and it was found that they resembled the parent compound with the following qualifications. (1) The two maxima of 7-azaindole have suffered a bathochromic shift. (2) A new absorption characteristic "A" has appeared, responsible for the colour of the compounds. (3) Where the group R absorbs in the ultra-violet region then there is a separate contribution due to this group. See table II, figure 1.

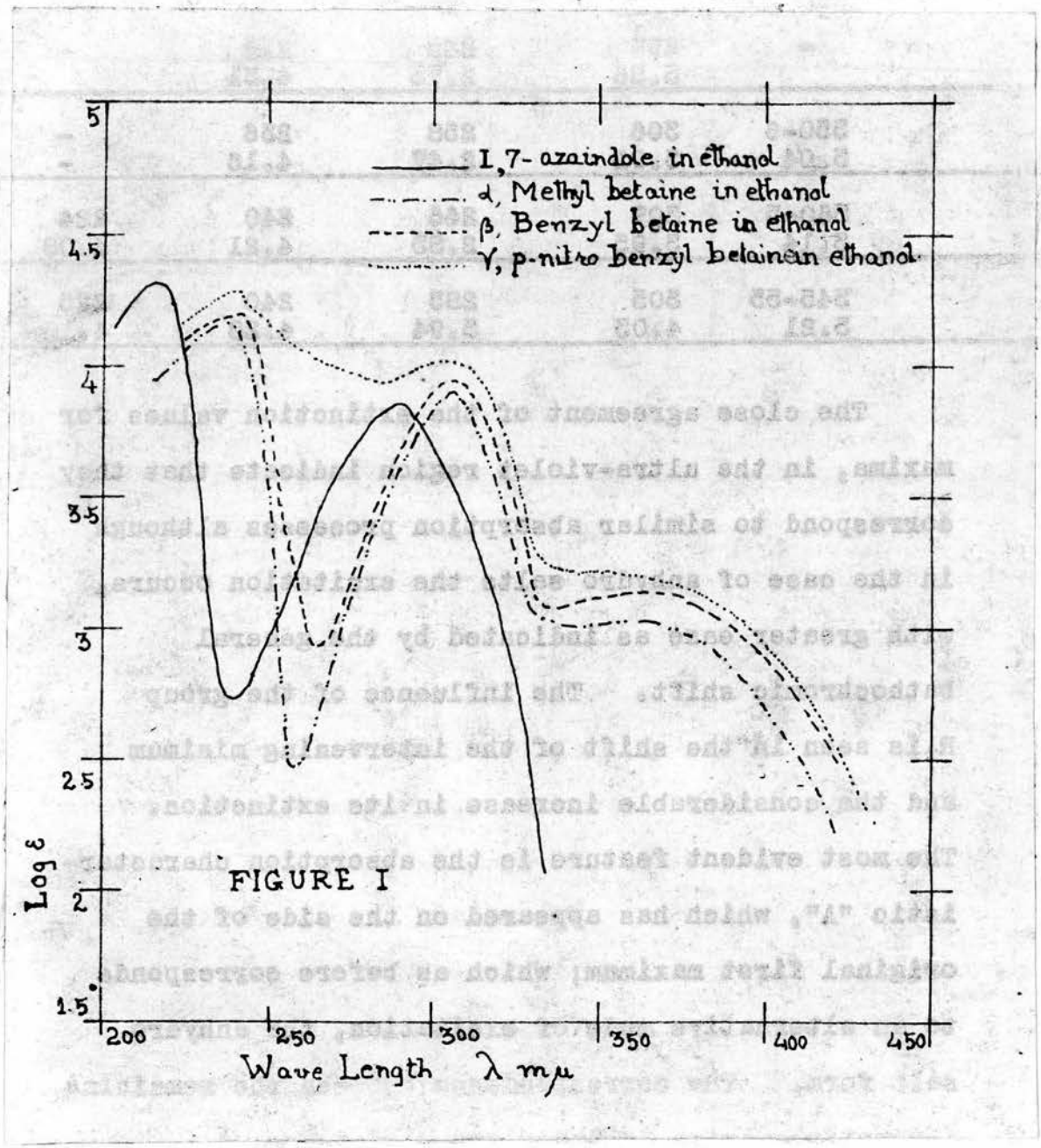

I, 7- azaindole in ethanol
α, Methyl betaine in ethanol
β, Benzyl betaine in ethanol
γ, p-nitro benzyl betainein ethanol
5
4.5
4
3.5
3
2.5
2
1.5
Log ε
200
250
300
350
400
450
Wave Length λ mμ

FIGURE I

Table II.

A

Compound	infl. mμ log ε	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε	λ min. mμ log ε
I	-	290 3.86	239 2.73	218 4.31	-
α	350-6 3.04	306 3.91	258 2.47	236 4.16	- -
β	360-5 3.14	307 3.95	266 2.83	240 4.21	224 4.08
γ	345-55 3.21	305 4.03	285 3.94	240 4.28	225 4.18

The close agreement of the extinction values for maxima, in the ultra-violet region indicate that they correspond to similar absorption processes although in the case of anhydro salts the excitation occurs, with greater ease as indicated by the general bathochromic shift. The influence of the group R is seen in the shift of the intervening minimum and the considerable increase in its extinction. The most evident feature is the absorption characteristic "A", which has appeared on the side of the original first maximum; which as before corresponds to an alternative mode of excitation, the anhydro salt form. The correspondence between the remaining absorption maxima in the ultra violet region indicates that there has been no fundamental change in the structural type, as would be indicated by the form II (a), and that the betaine formulation satisfies

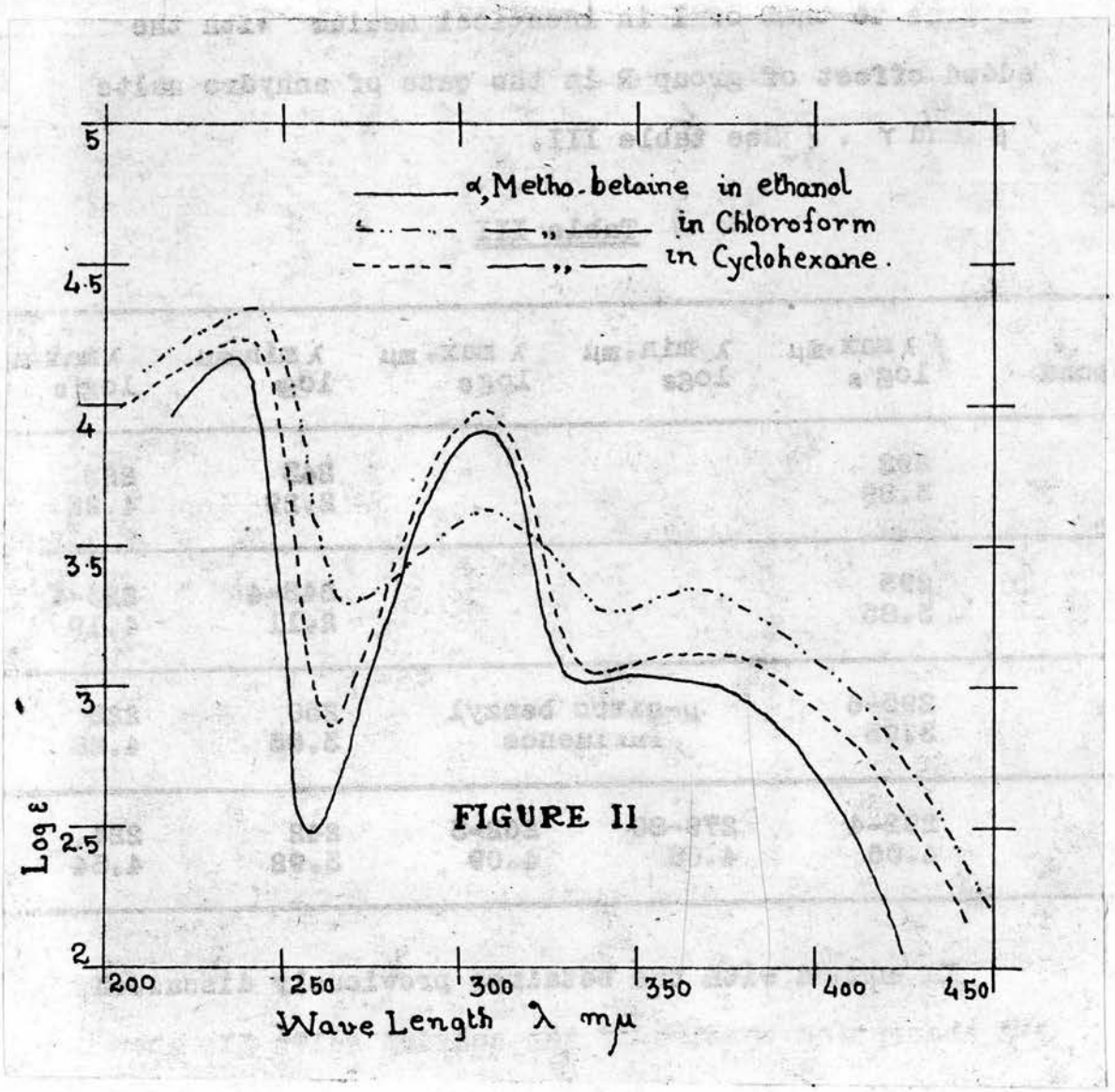

α, Metho-betaine in ethanol
,, in Chloroform
,, in Cyclohexane.
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
Wave Length λ mμ

FIGURE II

the requirements of the absorption spectra. The betaine structure, as it appears, is made apparent by a bathochromic shift of the normal absorption and the development of a new absorption band "A" in the higher wavelengths.

In acid solution as expected the absorption returns to that of I in identical medium with the added effect of group R in the case of anhydro salts β and γ . See table III.

Table III

Compound	λ max.mμ log ε	λ min.mμ log ε	λ max. mμ log ε	λ min.mμ log ε	λ max.mμ log ε
I	292 3.89			243 2.29	223 4.23
α	295 3.85			243-4 2.11	223-4 4.19
β	295-6 3.95	p-nitro benzyl influence		250 3.05	225 4.28
γ	292-4 4.06	279-80 4.03	262-3 4.09	242 3.92	224 4.34

In common with the betaines previously discussed, the absorption spectra of the anhydro salts II, show considerable dependence on the environment. Thus, their anhydro salt character "A" is affected by the two factors (a) that due to hydrogon-bonding (b) that due to dipolar interaction with the solvent

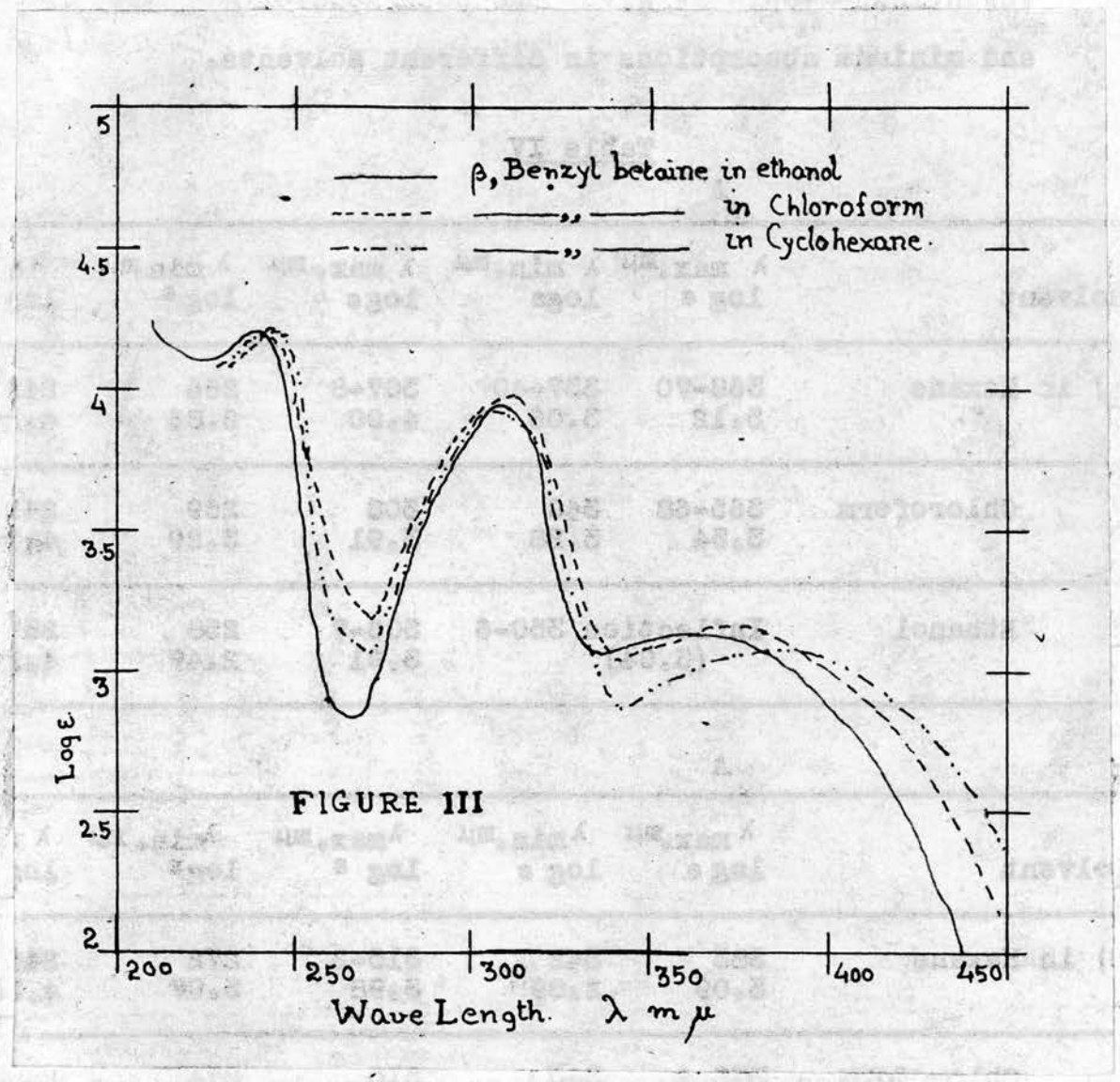

β, Benzyl betaine in ethanol
in Chloroform
in Cyclohexane
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
Wave Length. λ mμ

FIGURE III

molecules. These were studied by comparing the absorption spectra in ethanol, chloroform and hexane. In hexane, the environment will have minimal effect, so this was taken as the standard for estimation of variation. Table IV gives the positions of maximum and minimum absorptions in different solvents.

Table IV

A

Solvent	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε
(α) in Hexane	368-70 3.12	337-40 3.06	307-8 4.00	266 2.86	242 4.24
" Chloroform	365-68 3.34	340 3.28	308 3.91	269 3.29	242 4.34
" Ethanol	Inflection 350-6 (3.04)		306-7 3.91	258 2.47	237 4.16

A

Solvent	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε
(β) in Hexane	383 3.09	342 2.89	310-2 3.98	272 3.07	244 4.20
" Chloroform	373-4 3.17	340 3.06	310 4.1	274 3.37	242 4.19
" Ethanol	Inflection 360-5 (3.14)		307 3.95	266 2.83	240 4.21

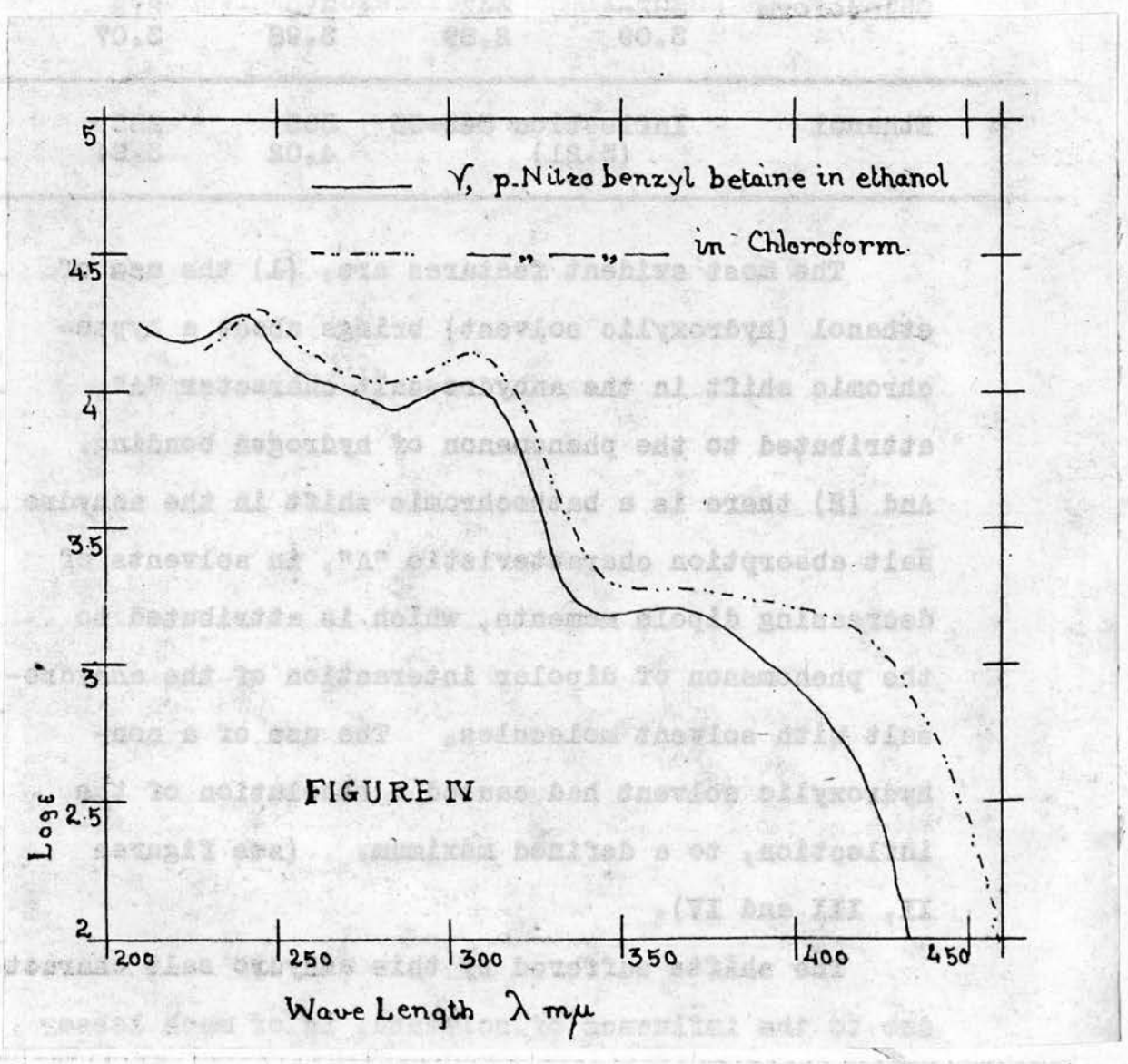

5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
450
Wave Length λ mμ
γ, p.Nitro benzyl betaine in ethanol
„ „ in Chloroform.

FIGURE IV

A

Solvent	λ max. mμ log ε	λ min. mμ log ε	λ max. mμ log ε	λ min. mμ log ε	λ max mμ log ε
(γ) in Hexane	Insoluble.				
" Chloroform	382-4 3.09	342 2.89	310 3.98	272 3.07	241 4.20
" Ethanol	Inflection 345-55 (3.21)		305 4.02	285 3.94	240 4.28

The most evident features are, (1) the use of ethanol (hydroxylic solvent) brings about a hypsochromic shift in the anhydro-salt character "A", attributed to the phenomenon of hydrogen bonding. And (2) there is a bathochromic shift in the anhydro salt absorption characteristic "A", in solvents of decreasing dipole moments, which is attributed to the phenomenon of dipolar interaction of the anhydro-salt with solvent molecules. The use of a non-hydroxylic solvent had caused a resolution of the inflection, to a defined maximum. (see figures II, III and IV).

The shifts suffered by this anhydro salt character, due to the influence of solvents, is of much lesser degree compared to that by phenol and enol betaines. This is probably due to comparative ease with which these $\overline{N}$-betaines are capable of reverting to purely covalent form II (a), which would not show any marked

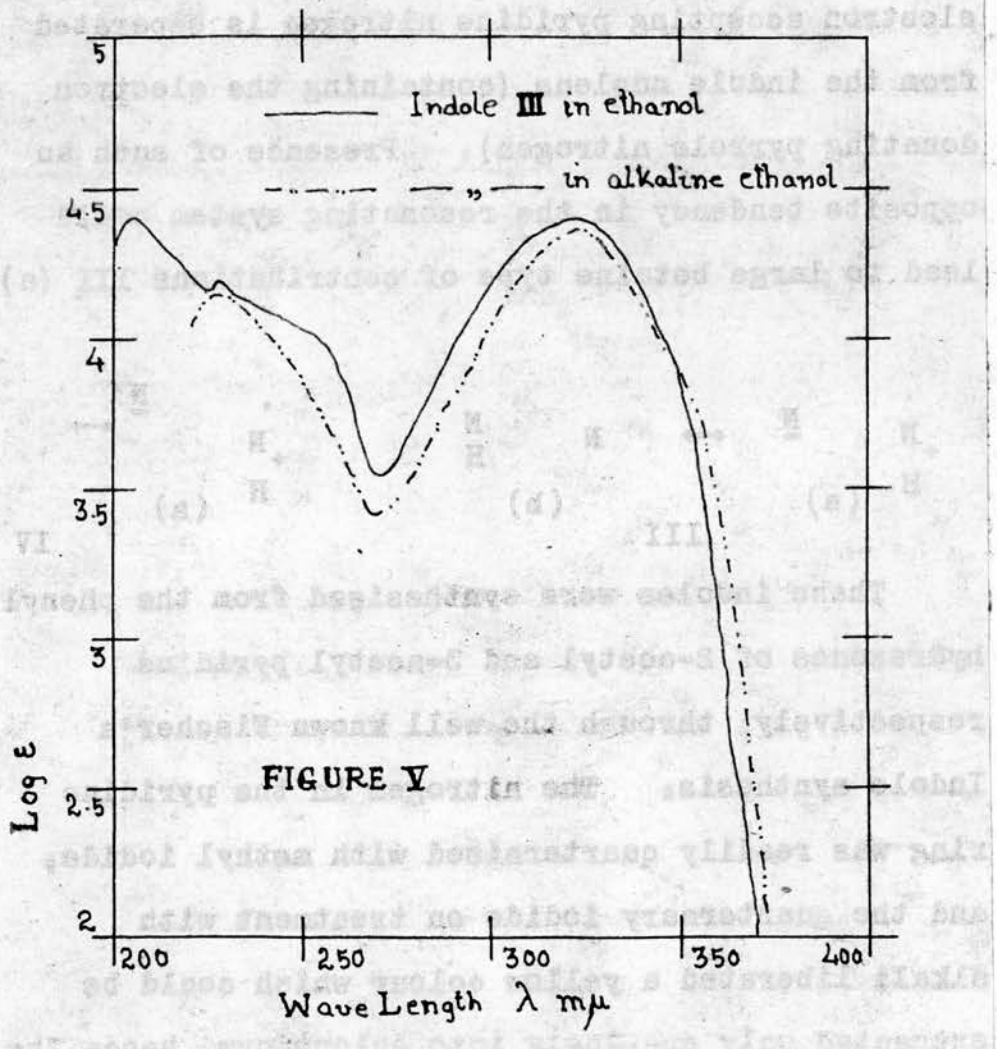
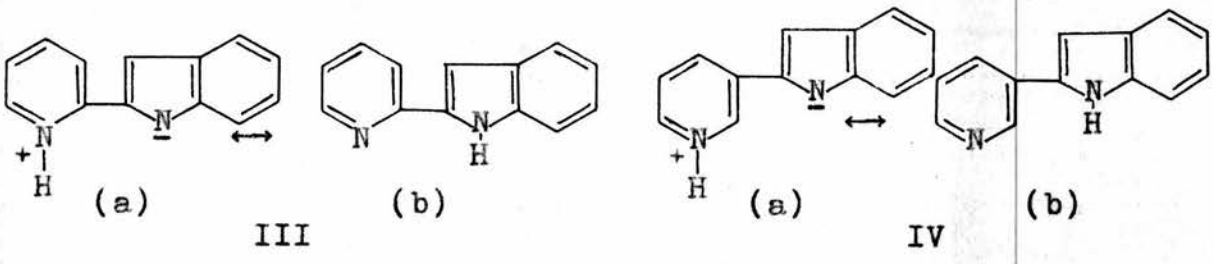

Indole III in ethanol
" in alkaline ethanol
5
4.5
4
3.5
3
2.5
2
Log ε
200
250
300
350
400
Wave Length λ mμ

FIGURE V

dependance on the solvent effect. This is also manifested by very slight alteration of absorption in the ultra violet region, taken in different solvents.

For comparitive purposes betaines from 2-pyridyl-indoles III and IV, were studied, in which the electron accepting pyridine nitrogen is separated from the indole nucleus (containing the electron donating pyrrole nitrogen). Presence of such an opposing tendency in the resonating system could lead to large betaine type of contributions III (a), IV (a).



These indoles were synthesised from the phenyl hydrazones of 2-acetyl and 3-acetyl pyridine respectively, through the well known Fischer's Indole synthesis. The nitrogen in the pyridine ring was readily quarternised with methyl iodide, and the quarternary iodide on treatment with alkali liberated a yellow colour which could be extracted only sparingly, into chloroform. Hence the betaines could not be isolated in pure form, and their spectra were studied from the solutions of corresponding methiodides in alkali. Table V gives the spectra of the two indoles and their methiodides

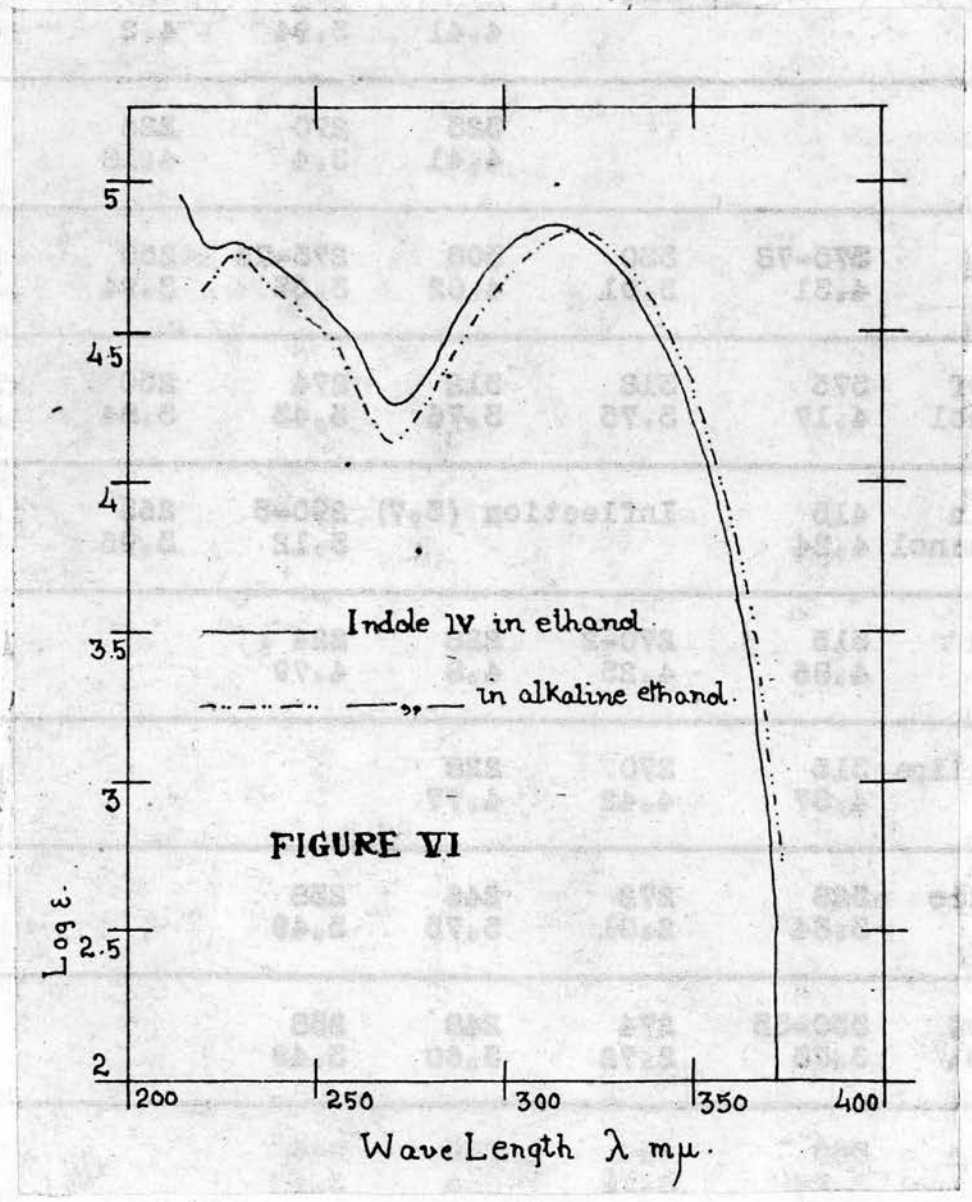

5
4.5
4
3.5
3
2.5
2
Log ε.
200
250
300
350
400
Wave Length λ mμ.
Indole IV in ethanol.
in alkaline ethanol.

FIGURE VI

in different media.

Table V

A

Solvent	λmax. log ε	λ min. logε	λ max. logε	λ min. log ε	λ max. log ε	λ min. logε	λ max. log ε
Indole III in ethanol	mμ	mμ	323 mμ 4.41	271 mμ 3.94	227 mμ 4.2	226 mμ 4.15	204 mμ 4.41
In alkaline ethanol			323 4.41	270 3.4	226 4.18		
In acidic ethanol	375-78 4.31	330 3.91	308 4.02	273-75 3.63	250 3.94	235 3.86	208 4.48
Methiodide of III in ethanol	375 4.17	318 3.75	312 3.76	274 3.43	250 3.84	245 3.82	213 4.57
Methiodide in alkaline ethanol	415 4.24	Inflection (3.7) 330-35		290-3 3.12	265 3.96	246 3.73	217 4.5
Indole IV in ethanol	315 4.86	270-2 4.25	228 4.8	224 4.79			
" in alkaline ethanol	315 4.87	270 4.42	228 4.77				
" in acidic ethanol	328 3.84	272 2.81	246 3.75	238 3.49			
Methiodide of IV in ethanol	330-33 3.73	274 2.72	248 3.60	238 3.49			
Methiodide in alkaline ethanol	360 3.67	280 2.79	246 3.6	244 3.58			

The spectra of the two indoles are identical, and are not altered by the alkalinity of the solvent.

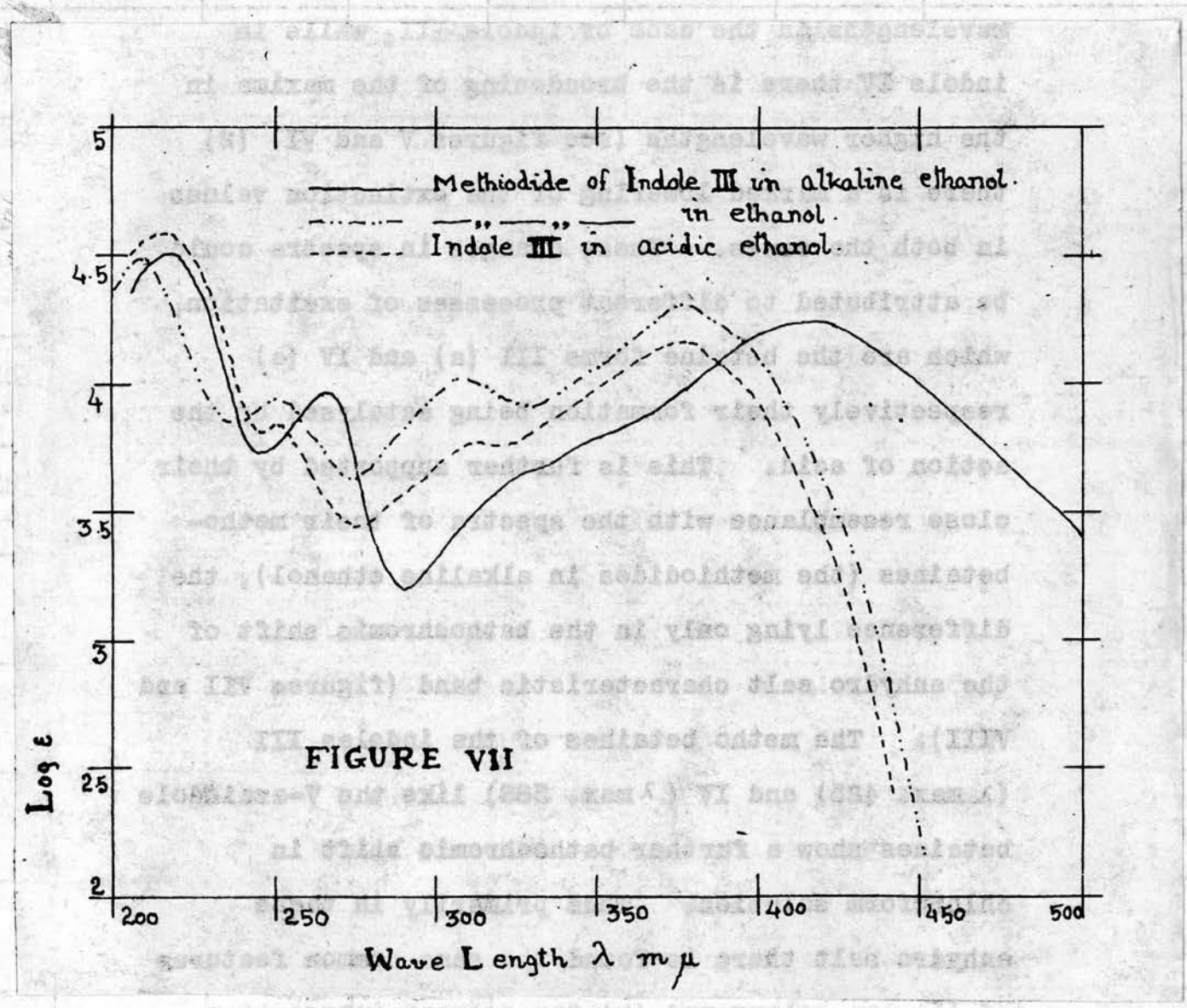

Methiodide of Indole III in alkaline ethanol.
" " " in ethanol.
Indole III in acidic ethanol.
Log ε
5
4.5
4
3.5
3
2.5
2
200
250
300
350
400
450
500
Wave Length λ mμ

FIGURE VII

In the acidic medium, as well as on quarternisation, however, their spectra (which as expected are identical), are considerably altered in two ways (1) There appears a new absorption maximum in the higher wavelengths in the case of the indole III, while in indole IV there is the broadening of the maxima in the higher wavelengths (see figures V and VI). (2) There is a marked lowering of the extinction values in both the cases. These changes in spectra could be attributed to different processes of excitation, which are the betaine forms III (a) and IV (a) respectively, their formation being catalysed by the action of acid. This is further supported by their close resemblance with the spectra of their metho-betaines (the methiodides in alkaline ethanol), the difference lying only in the bathochromic shift of the anhydro salt characteristic band (figures VII and VIII). The metho betaines of the indoles III, (λ max. 425), and IV, (λ max. 388), like the 7-azaindole betaines show a further bathochromic shift in chloroform solution. Thus primarily in these anhydro salts there is found the same common features of, (1) low colour and (2) the solvent interaction.

Anhydro-salt derivatives of α- and β-carboline:- Anhydro-salts derived from α- and β-carbolines have been included in this section, because the same resonance of electron accepting pyridine

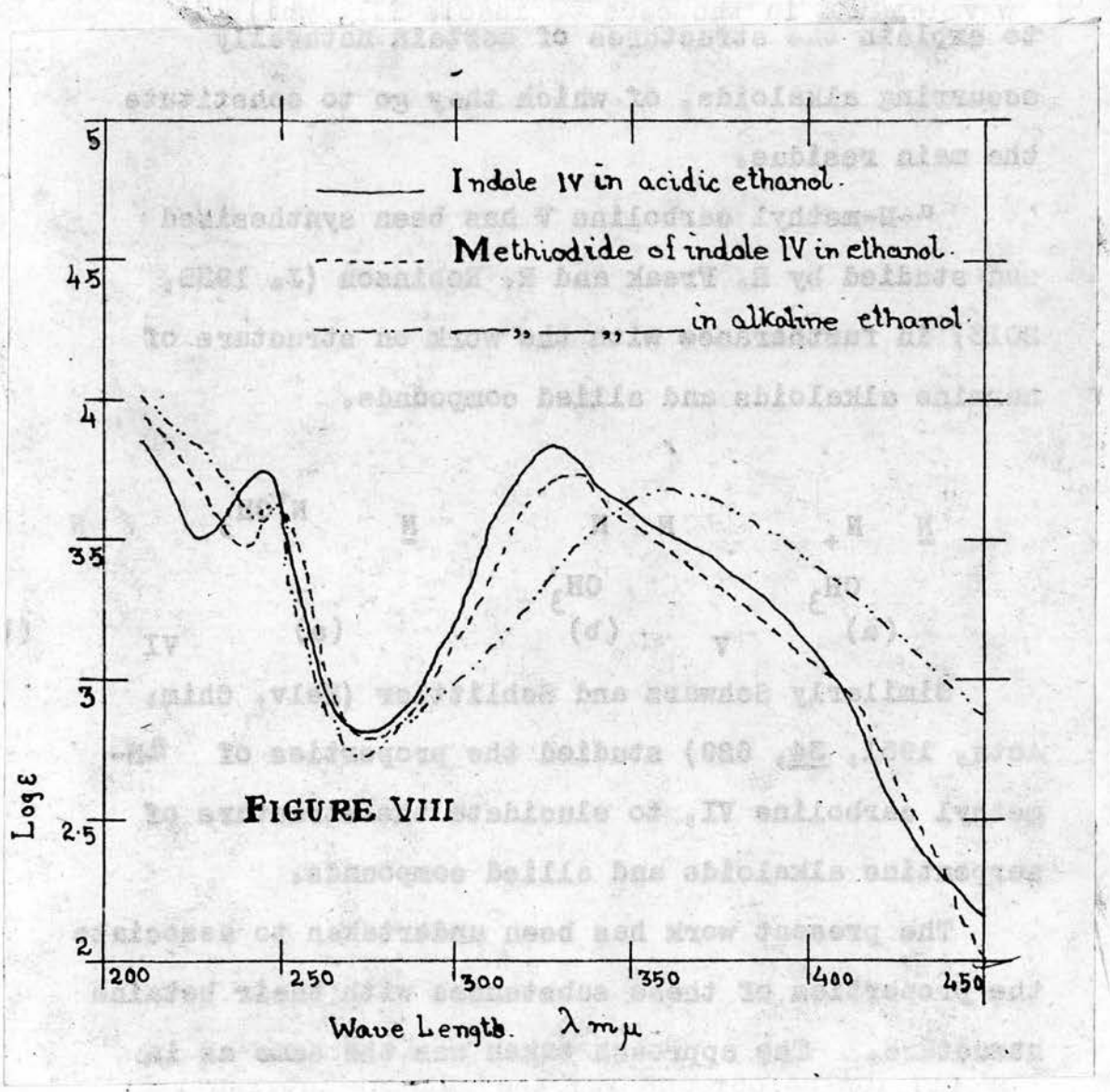
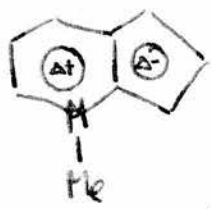
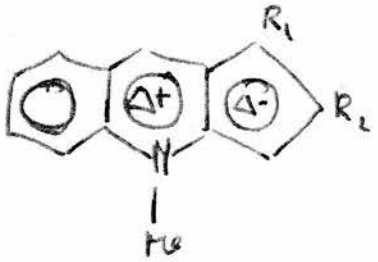

Indole IV in acidic ethanol.
Methiodide of indole IV in ethanol.
" " " in alkaline ethanol.
5
4·5
4
3·5
3
2·5
2
Log ε
200
250
300
350
400
450
Wave Length. λ mμ

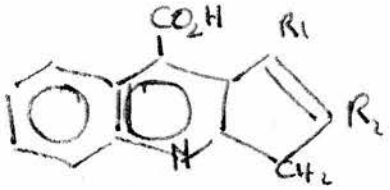
FIGURE VIII

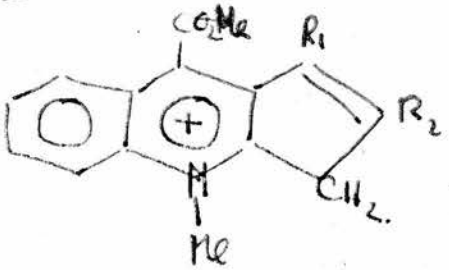


I



II ($R_1 = R_2 = H$)
V ($R_1 = H$; $R_2 = Ph$)
VI. ($R_1 = R_2 = Ph$).

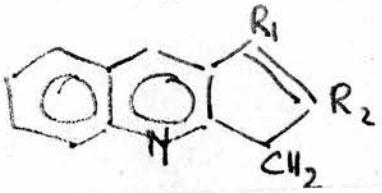


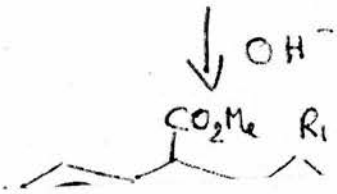


I⁻

① EtOH/H_2SO_4
② MeI

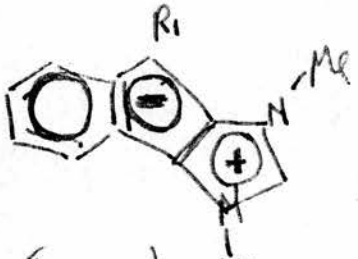
CH_2N_2



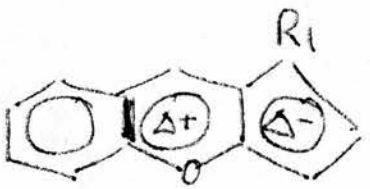


V ~~VI~~ V. ($R_1 = H$)
VI ($R_1 = Ph$).

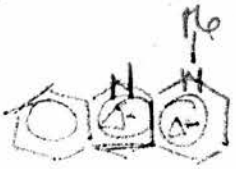
III. $R_1 = H$, $R_2 = Ph$.
IV $R_1 = R_2 = Ph$.

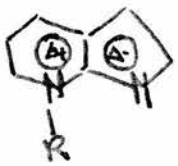


IX ($R_1 = H$)
X ($R_1 = Ph$).

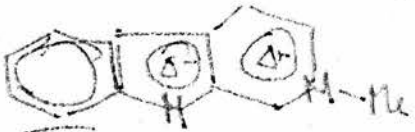


VII ($R_1 = H$; $R_2 = Ph$)
VIII ($R_1 = R_2 = Ph$)





XI R = Me
XII R = $Ph.CH_2$.
XIII R = $Ph\text{-}NO_2$; Ph. etc.

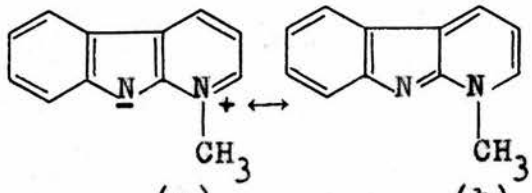


XIV

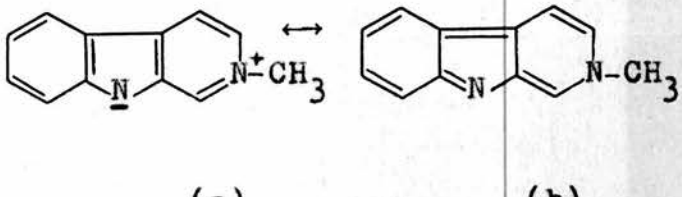
nitrogen and electron donating pyrrole nitrogen systems are involved in them, as in the previously discussed anhydro-salts.

The coloured anhydro-salts derived from α- and β- carboline have been made and studied, in order to explain the structures of certain naturally occurring alkaloids, of which they go to constitute the main residue.

α-N-methyl carboline V has been synthesised and studied by R. Freak and R. Robinson (J., 1938, 2013), in furtherance with the work on structure of harmine alkaloids and allied compounds.



(a) V (b)



(a) VI (b)

Similarly Schwarz and Schlittler (Helv. Chim. Acta, 1951, 34, 629) studied the properties of β-N-methyl carboline, VI, to elucidate the structure of serpentine alkaloids and allied compounds.

The present work has been undertaken to associate the properties of these substances with their betaine structure. The approach taken was the same as in the other N̄-betaines.

The influence of solvent interaction upon the anhydro salts V and VI was studied spectroscopically. The results that were obtained are tabulated below.

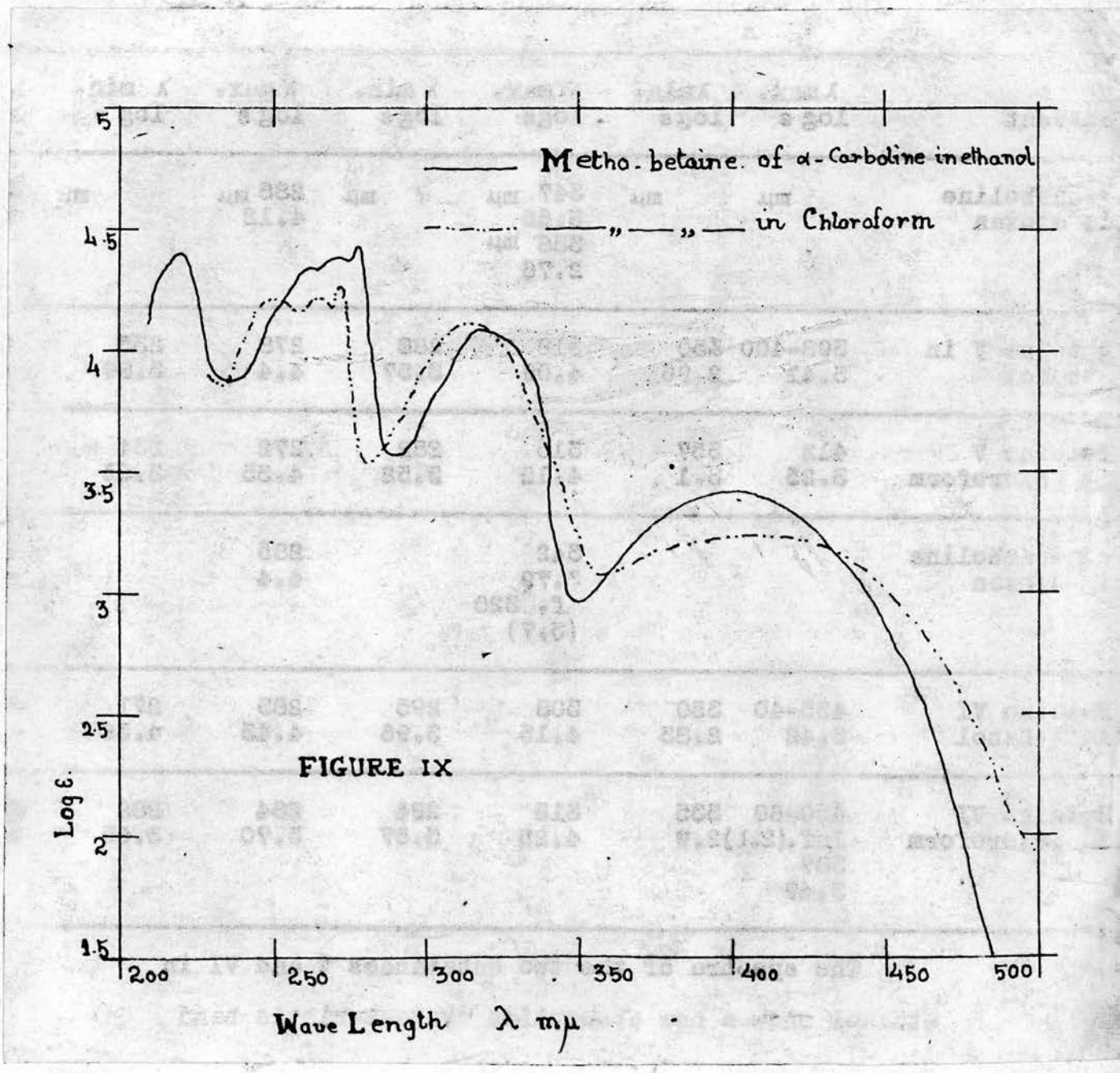

Metho. betaine of α-Carboline in ethanol
,, ,, in Chloroform
5
4.5
4
3.5
3
2.5
2
1.5
Log ε.
200
250
300
350
400
450
500
Wave Length λ mμ

FIGURE IX

The spectrum of the parent base, for comparison was taken from (Horner, Annalen, 1939, 540, 77).

Table VI

A

Solvent	λmax. log ε	λmin. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
α-carboline in dioxan	mμ	mμ	347 mμ 3.66 338 mμ 2.76	mμ	288 mμ 4.12	mμ	225-30mμ 4.56
Betaine V in ethanol	398-400 3.41	350 2.96	318 4.09	288 3.57	278 4.4	235 3.89	220 4.41
Betaine V in chloroform	412 3.25	357 3.1	315 4.15	282 3.52	272 4.35	234 3.85	
β -carboline in dioxan			342 3.79 Inf. 328 (3.7)		285 4.4		220-30 4.7
Betaine VI in ethanol	435-40 3.42	350 2.83	308 4.15	295 3.96	283 4.43	271 4.36	262 4.42
Betaine VI in chloroform	450-60 Inf.(2.1) 387 3.49	335 2.9	313 4.25	294 3.67	284 3.70	282 3.65	266 4.37

The spectra of the two substances V and VI in ethanol show a new absorption characteristic band "A", not present in the parent base. This is attributed to the different absorption process of excitation, which is the anhydro-salt form. The spectra in the ultra violet region are shifted,

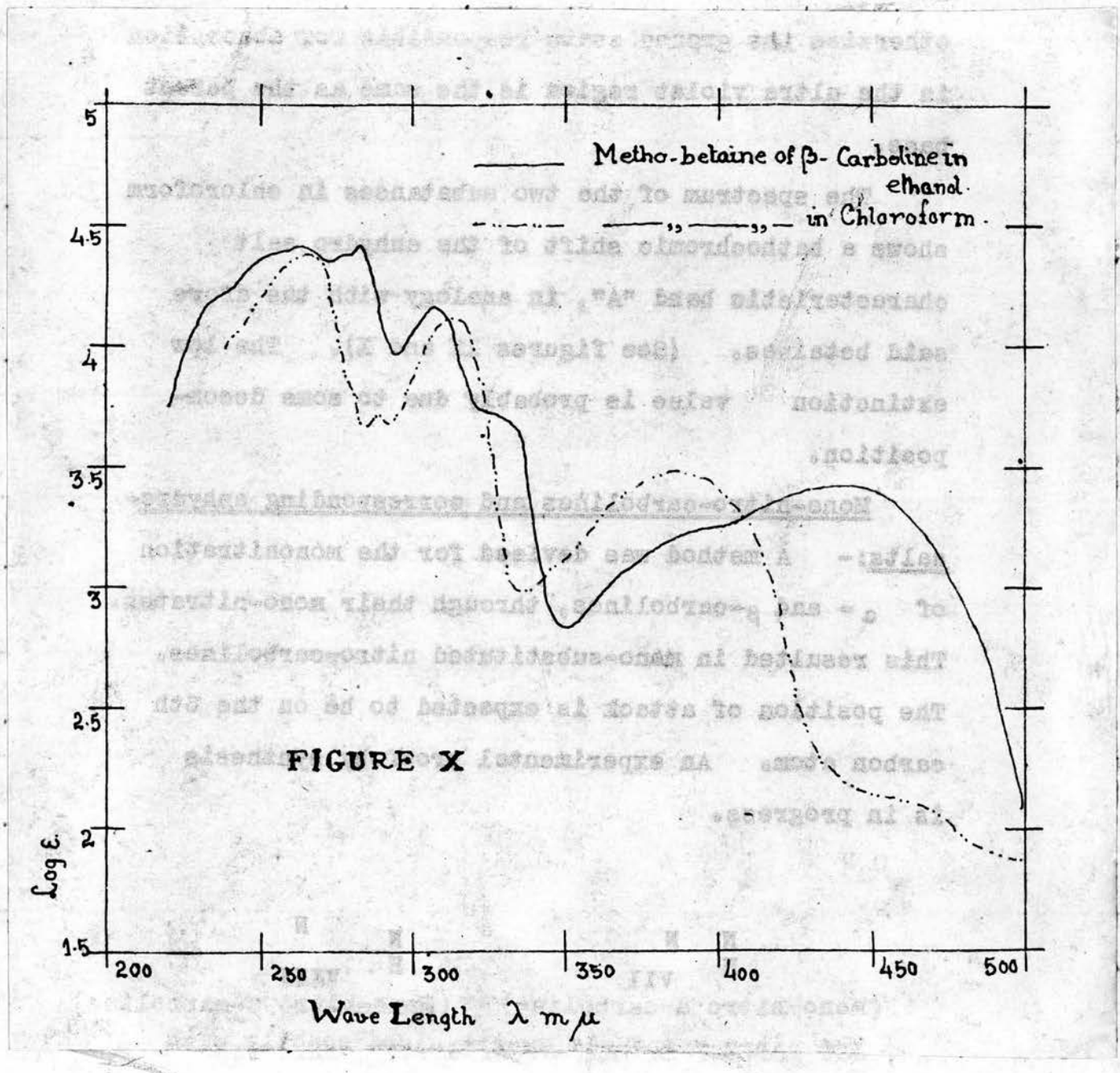
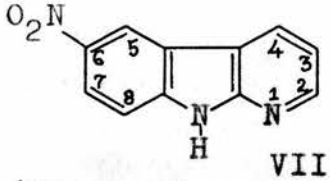

Metho-betaine of β- Carboline in ethanol.
,, ,, in Chloroform.
5
4.5
4
3.5
3
2.5
2
1.5
Log ε
200
250
300
350
400
450
500
Wave Length λ mμ

FIGURE X

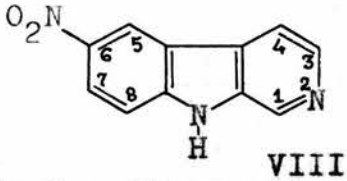
hypsochromically though the characteristic absorption features are not markedly altered as shown by the close agreement of extinction values. The difference is attributed to the different pH of the medium, otherwise the ground state responsible for absorption in the ultra violet region is the same as the parent base.

The spectrum of the two substances in chloroform shows a bathochromic shift of the anhydro salt characteristic band "A", in analogy with the afore said betaines. (See figures IX and X). The low extinction [illegible] value is probably due to some decomposition.

Mono-nitro-carbolines and corresponding anhydro-salts:- A method was devised for the mononitration of α- and β-carbolines, through their mono-nitrates. This resulted in mono-substituted nitro-carbolines. The position of attack is expected to be on the 6th carbon atom. An experimental proof by synthesis is in progress.



VII
(Mono-nitro α-carboline)



VIII
(Mono-nitro β-carboline)

The nitro compounds quarternised readily with methyl iodide, which yielded stable anhydro-salts on treatment with alkali, analysing correctly for the betaines.

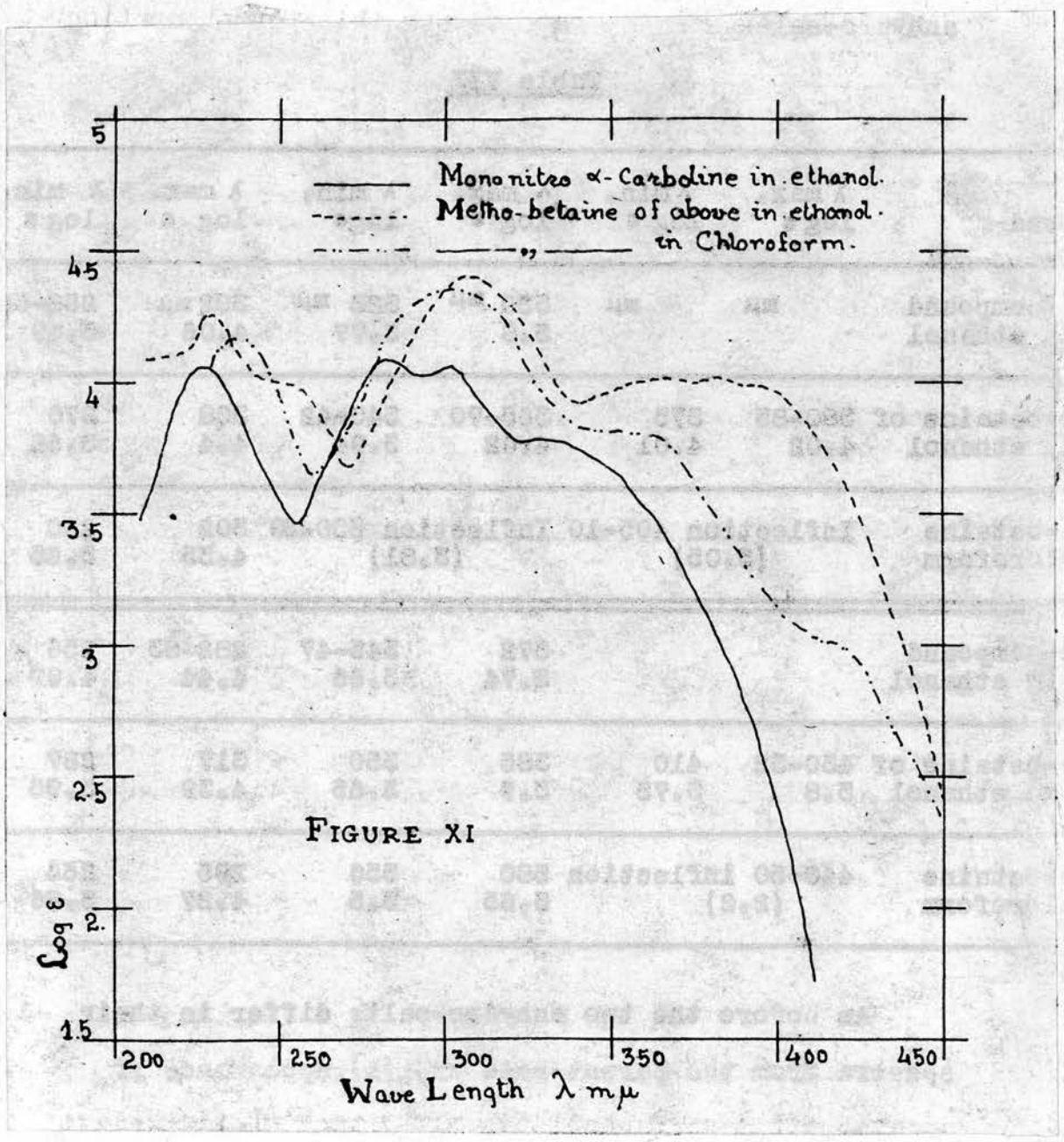

Mononitro α-Carboline in ethanol.
Metho-betaine of above in ethanol.
" " in Chloroform.
5
4.5
4
3.5
3
2.5
2.
1.5
Log ε
200
250
300
350
400
450
Wave Length λ mμ

FIGURE XI

The two betaines were examined spectroscopically, in different solvents, to investigate the solvent effect on their anhydro-salt structure. Table VII gives the spectra of the parent bases and their anhydro-salts.

Table VII

A

Compound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
Nitro-compound VII in ethanol	mμ	mμ	330 mμ 3.8	323 mμ 3.77	302 mμ 4.06	258-56mμ 3.49	228 mμ 4.06
Metho-betaine of VII in ethanol	380-85 4.02	375 4.01	365-70 4.02	340-42 3.94	308 4.4	270 3.68	229-30 4.56
Metho-betaine in chloroform	Inflection 405-10 (3.05)		Inflection 350-60 (3.81)		302 4.35	260 3.65	238 4.17
Nitro-compound VIII in ethanol			372 3.74	345-47 3.66	282-83 4.44	256 4.07	238 4.38
Metho-betaine of VIII in ethanol	430-32 3.8	410 3.73	385 3.9	350 3.65	317 4.39	287 3.96	259 4.39
Metho-betaine in chloroform	448-50 inflection (2.2)		380 3.65	356 3.5	295 4.27	266 3.86	246 4.17

As before the two anhydro-salts differ in their spectrumfrom the parent base in,(1) the appearance of an absorption characteristic "A", which is influenced by hydrogen bonding and polar interaction with the environments and, (2) the spectrum in the ultra violet region is bathochromically shifted, although the

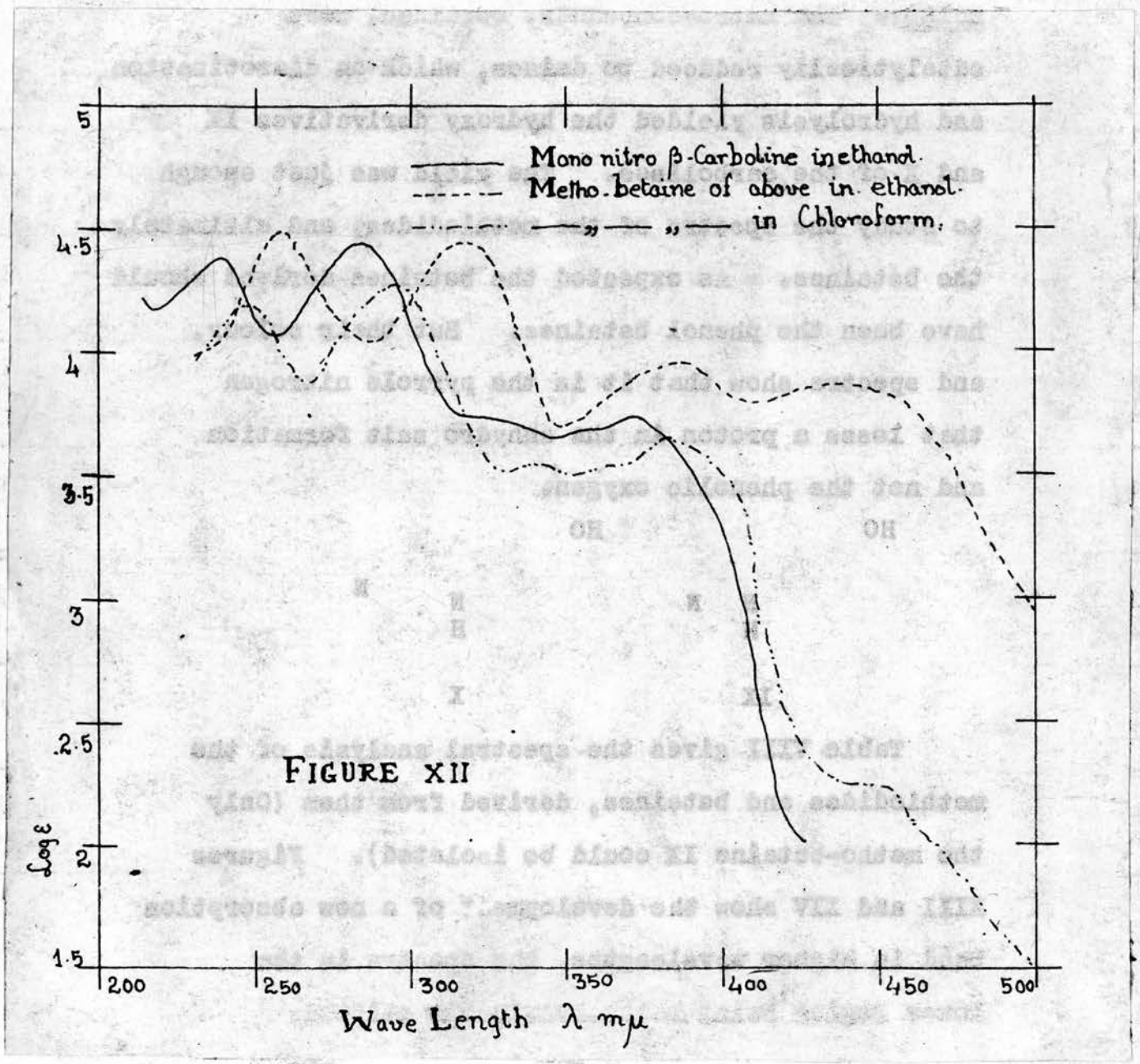
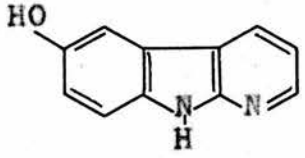

Mono nitro β-Carboline in ethanol.
Metho. betaine of above in ethanol.
„ „ in Chloroform.
5
4·5
4
3·5
3
2·5
2
1·5
Log ε
200
250
300
350
400
450
500
Wave Length λ mμ

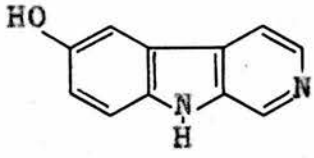
FIGURE XII

close correspondance of the extinction values in maxima and minima, suggest the sameness of the excitation process (see figures XI and XII).

Hydroxy-carbolines and corresponding anhydro-salts:- The nitro-compounds, obtained, were catalytically reduced to amines, which on diazotisation and hydrolysis yielded the hydroxy derivatives(IX and X)of the carbolines. The yield was just enough to study the spectra of the methiodides, and ultimately the betaines. As expected the betaines derived should have been the phenol betaines. But their colour, and spectra show that it is the pyrrole nitrogen that loses a proton in the anhydro salt formation and not the phenolic oxygen.



IX



X

Table VIII gives the spectral analysis of the methiodides and the betaines, derived from them (Only the metho-betaine IX could be isolated). Figures XIII and XIV show the development of a new absorption band in higher wavelengths, the spectrum in the lower region being bathochromically shifted.

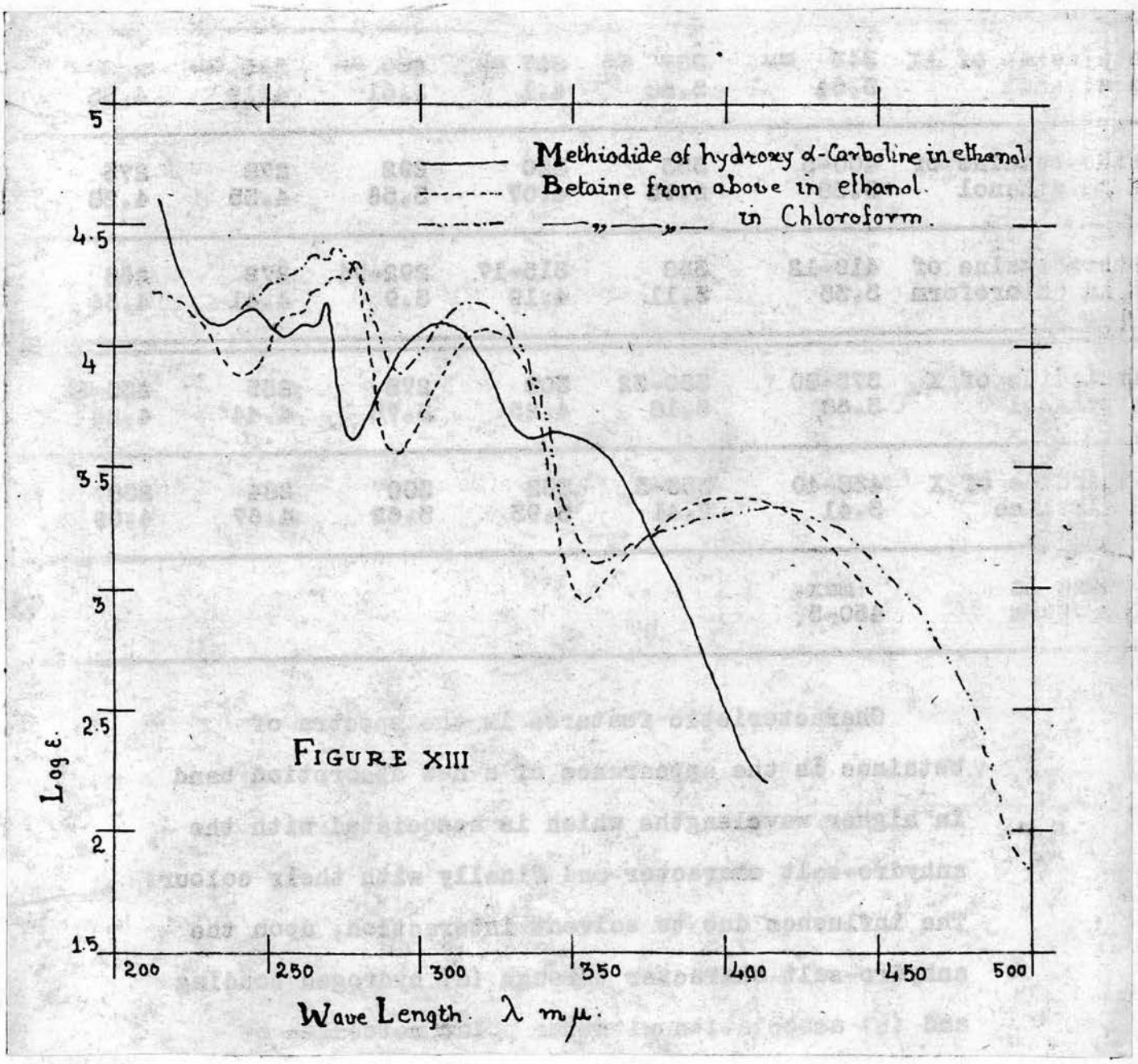

Methiodide of hydroxy α-Carboline in ethanol.
Betaine from above in ethanol.
„ „ in Chloroform.
5
4.5
4
3.5
3
2.5
2
1.5
Log ε.
200
250
300
350
400
450
500
Wave Length λ mμ.

FIGURE XIII

Table VIII

Compound	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε	λ min. log ε	λ max. log ε
ethiodide of IX n ethanol	345 mμ 3.64	337 mμ 3.63	307 mμ 4.1	280 mμ 3.61	269 mμ 4.19	256 mμ 4.03	244 mμ 4.16
etho-betaine of X in ethanol	400-5 3.38	353 2.95	320 4.07	292 3.56	278 4.35	275 4.28	268-70 4.35
etho-betaine of X in chloroform	410-12 3.33	358 3.11	315-17 4.19	292-94 3.9	272 4.41	268 4.36	266 4.37
ethiodide of X n ethanol	375-80 3.68	330-32 3.18	308 4.25	278 3.75	255 4.44	235-36 4.26	218-19 4.39
ethiodide of X n alkaline thanol	438-40 3.41	353-5 2.41	332 3.93	300 3.62	284 4.67	238 4.09	214 4.56
etaine in hloroform	max. 450-5						

Characteristic features in the spectra of betaines is the appearance of a new absorption band in higher wavelengths, which is associated with the anhydro-salt character, and finally with their colour. The influence due to solvent interaction, upon the anhydro-salt character through (a) hydrogen bonding and (b) association with the polar molecules of solvents, reflects upon the salt like structure of the substances.

A hypsochromic shift due to hydrogen bonding shows that the anhydro salt character is getting

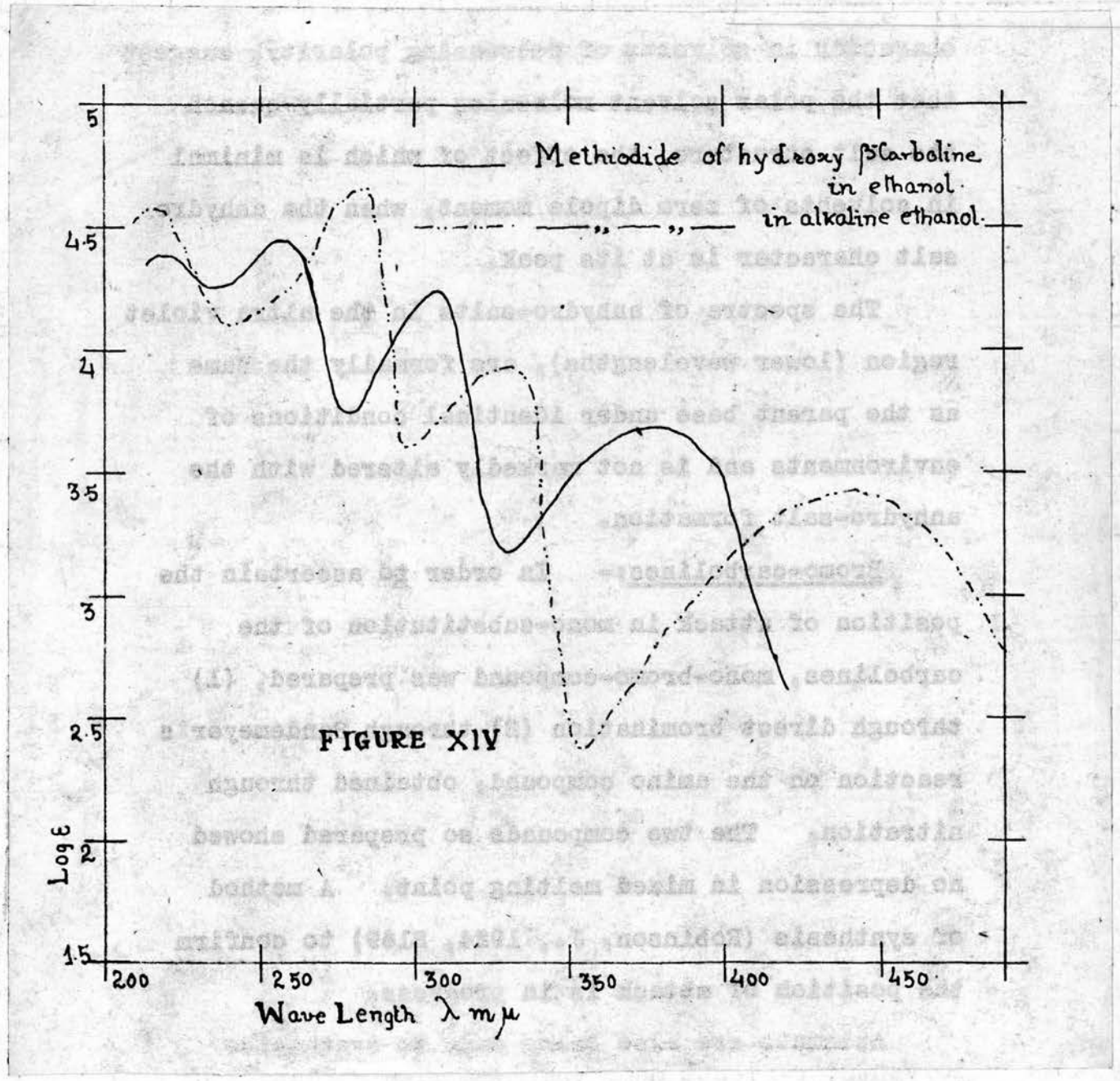

Methiodide of hydroxy βCarboline
in ethanol
in alkaline ethanol
5
4.5
4
3.5
3
2.5
2
1.5
Log ε
200
250
300
350
400
450
Wave Length λ mμ

FIGURE XIV

partially neutralised, which ceases to exist in acid solution, where hydrogen is retained by the anion in a strong covalent linkage.

A bathochromic shift of the anhydro salt character in solvents of decreasing polarity, suggests that the polar solvent molecules partially quench the salt structure, the effect of which is minimal in solvents of zero dipole moment, when the anhydro salt character is at its peak.

The spectra of anhydro-salts in the ultra violet region (lower wavelengths), are formally the same as the parent base under identical conditions of environments and is not markedly altered with the anhydro-salt formation.

Bromo-carbolines:- In order to ascertain the position of attack in mono-substitution of the carbolines, mono-bromo-compound was prepared, (1) through direct bromination (2) through Sandemeyer's reaction on the amino compound, obtained through nitration. The two compounds so prepared showed no depression in mixed melting point. A method of synthesis (Robinson, J., 1924, 2169) to confirm the position of attack is in progress.

Attempts are also being made to synthesise hydroxy-phenyl substituted carbolines, through condensation of dl-tryptophane with hydroxy-benzaldehydes (cf. β-carboline, Speitel and Schlittler,

Helv. Chim. Acta, 1949, 32, 860) to study the anhydro salts derived from them; for comparison with the naturally occuring serpentine alkaloids.

Experimental

Quarternary salts of 7-azaindole:- These salts were all made in the same way. 7-azaindole was dissolved in Analar acetone and excess of the desired alkyl halide was added. The solution was boiled under reflux for two hours, when the separation of the quarternary salt was complete. After cooling, the solid was filtered and washed with ether, to remove excess of alkyl halide. The derivative was purified, by crystallising it from a minimum volume of alcohol by the addition of ether. The yields were quantitative.

7-methyl-7-azaindolium iodide:- This was made by refluxing methyl iodide with 7-azaindole. The compound crystallised out as long white needles. M.P. 154-55°C. It forms a crystalline yellow picrate M.P. 210°C. Analysis of the quarternary salt shows the presence of one molecule of water of crystallisation C = 34.0%, H = 3.72%, N = 9.8%, I = 45% (found) and C = 34.5%, H = 3.95%, N = 10.01%, I = 45.5% (calculated for $C_8H_9N_2I + H_2O$)

7-Benzyl-7-azaindolium chloride:- This was the condensation product of 7-azaindole with benzyl chloride. It crystallised out as white needles M.P. 162°C. Analysis, chlorine = 15% (found), and 14.6% (required).

7-p-nitrobenzyl-7-azaindolium bromide:- This was

the condensation product of 7-azaindole with p-nitro benzyl bromide. It was obtained as colourless needles. M.P. 200°C.

Analysis:- Bromine = 24.1% (found), and 24% (calculated).

Derivation of anhydro salts from the quarternary compounds:- The preparation of these substances followed a similar pattern. The quarternary halides were dissolved in water, and the solution was made alkaline with potassium carbonate solution. The intense yellow colour produced was extracted into chloroform. After drying the solution over anhydrous sodium sulphate, it was concentrated, and the substances were crystallised by the addition of petrol. The 7-methyl-7-azaindolium hydroxide anhydro salt was slow to crystallise, and petrol alone was needed here. The compounds were obtained in good yields and readily crystallised.

7-methyl-7-azaindolium hydroxide anhydro salt:- The compound is less readily soluble in water and was wholly extracted into chloroform after two extractions. It crystallised out as yellow plates from (80-100°) petrol, M.P. 44°C. It forms a crystalline yellow picrate M.P. 210°C. (same as from the methiodide). The betaine failed to analyse due to its immense affinity for moisture. The picrate analysed as Nitrogen = 19.4% (found) and 19.5% (calculated).

7-benzyl-7-azaindolium hydroxide anhydro salt:- This was sparingly soluble in water and was fully

extracted into chloroform. It was obtained as crystalline yellow needles from chloroform petrol mixture. M.P. 83°C.

Analysis C = 80.5%, H = 5.5%, N = 14% (found)

C = 80.7%, H = 5.7%, N = 13.5% (calculated).

This betaine forms a yellow picrate M.P. 170°C.

Analysis N = 15.7% (found)

N = 16% (calculated)

7-p-nitrobenzyl-7-azaindolium hydroxide anhydro salt:- This was insoluble in water and was fully extracted into chloroform. The compound crystallised as fine yellow needles from chloroform petrol mixture M.P. 167°C.

Analysis C = 67%, H = 4.5%, N = 15.9% (found)

C = 66.4%, H = 4.4%, N = 16% (calculated)

Picrate M.P. 206°C.

Analysis N = 17.2%, (found)

N = 17.4%, (calculated)

1:7 dimethyl-7-azaindolium iodide:- The betaine 7-methyl-7-azaindolium hydroxide anhydro salt on refluxing with methyl iodide in analar acetone, yielded white needle shaped quarternary compound, which was crystallised from ethanol. M.P. 275°C.

Analysis

C = 39.8%, H = 4.0%, N = 9.5%, I = 46% (found)

C = 39.4%, H = 4.0%, N = 10.2%, I = 46.4% (calculated)

Preparation of phenyl hydrazones of 2- and 3-acetyl pyridine:- 4.84 gms. of an acetyl pyridine and 4.32 gms. of phenyl hydrazine in 30 mls. of ethyl alcohol, together with a few drops of glacial acetic acid, were boiled under reflux, for one hour. On cooling the solution turned turbid and pale white needles separated. These were recrystallised from 50 mls. of ethyl alcohol.

2-acetyl pyridine phenyl hydrazone:- It was obtained as pale white needles. M.P. 156°C. Yield 7.3 gms.

3-acetyl pyridine pheny hydrazone:- This was obtained as pale white needles. M.P. 146°C. Yield 7.5 gms.

The indole synthesis from the phenyl hydrazones

The methods of cyclisation (Chem. Reviews, 1942, 30, 78) of the phenyl hydrazones by boiling with glacial acetic, and boiling with zinc chloride and glacial acetic acid failed to bring about any change in the above compounds.

The compound was mixed intimately with equal amount of fused zinc chloride. It was heated at a temperature of 200 to 210°C. in an oil bath, for two hours when there was no more evolution of NH_3 (detected by litmus paper). The melt was allowed to cool and solidify. The zinc chloride complex was decomposed by boiling with 2N.NaOH solution. The product was

extracted with benzene and chromatographed on alumina. A yellow fluorescent band separated which was eluted with 50% petrol-benzene mixture. The indoles were finally crystallised with petrol (80-100°C.)

The yield of indole from 2-acetyl pyridine phenyl-hydrazone was 60% of the theoretical. The indole crystallised as white needles which sublimed and melted at 152°C. The mixed melting point with phenyl hydrazone was considerably depressed. The indole forms a picrate. M.P. 244°C.

Analysis of Indole.

C = 80.0%, H = 5.4%, N = 14.0% (found)

C = 80.4%, H = 5.2%, N = 14.4% (calculated)

Picrate of the Indole.

N = 17.20% (found)

N = 16.6% (calculated)

The yield of Indole from 3-acetyl pyridine phenyl-hydrazone was recorded as 76% of the theoretical. The indole crystallised from Petrol (80-100°C.) as white prisms M.P. 174°C. It also forms a picrate M.P. 195°C.

Analysis of Indole.

C = 79.8%, H = 5.2%, N = 14.9% (found)

C = 80.4%, H = 5.2%, N = 14.4% (calculated)

Picrate. N = 16.8% (found)

N = 16.6% (calculated).

Preparation of the methiodides of the 2'and 3'Pyridyl 2-Indoles:-

2-(2'-Pyridyl) Indole Methiodide:- The indole was dissolved in analar acetone and refluxed on the water bath with excess of methyl iodide. The methiodide did not separate even after a period of 24 hours of refluxing. Next time the indole was dissolved in methanol and the solution was boiled vigorously with excess of methyl iodide for 8 hours. The yellow methiodide of the indole separated. Excess of the solvent and methyliodide were distilled off and the compound was recrystallised from ethanol and ether as yellow needles. M.P. 235°C. (with decomposition).

Analysis.

C = 50.2%, H = 3.9%, N = 7.6%, I = 37.6% (found)

C = 50.0%, H = 3.9%, N = 8.3%, I = 37.7% (calculated)

2-(3'-Pyridyl) Indole Methiodide:- The indole was dissolved in analar acetone and methyl iodide was added in excess. The mixture was allowed to boil under reflux on the water bath for one hour. The pale yellow crystals of the methiodide separated. These were filtered and crystallised from ethanol as yellow needles. M.P. 245°C.

Analysis.

C = 50.5%, H = 4.1%, N = 8.0%, I = 37.7% (found)

C = 50.0%, H = 3.9%, N = 8.3%, I = 37.7% (calculated)

Liberation of the betaines from the methiodides:-

2-(2'-Pyridyl) Indole methiodide on treatment with 2 N. potassium carbonate solution liberated a yellow coloured betaine which could be extracted into chloroform in which it was fairly soluble. The betaine tends to decompose slowly on heating and keeping for a long time.

2-(3'-Pyridyl) Indole methiodide gives a yellow coloured betaine as well, on treatment with 2 N. sodium hydroxide solution. The betaine is sparingly soluble in chloroform and decomposes more readily than the previous betaine.

Neither of these betaines could be isolated in crystalline form.

Compounds of α- and β-Carboline (1-aza-carbazole and 2-aza-carbazole):- The desired aza-carbazole was dissolved in analar acetone, and was boiled under reflux, with excess of methyl iodide. After half an hour white solid separated, when the quarternisation was complete. Acetone and methyl iodide were distilled off, and the residual solid was crystallised from ethanol. Yield was quantitative.

Methiodide of 1-azacarbazole was obtained as white needles M.P. 224°C.

Analysis

C = 44.3%, H = 3.7%, N = 8.5%, I = 38.5% (found)

C = 43.9%, H = 3.96%, N = 8.5%, I = 38.8%

(calculated for $C_{12}H_{11}N_2I$ - H_2O

The metho betaine on further refluxing with methyl iodide in analar acetone, for half an hour, yielded a white crystalline methiode. It crystallised from ethanol as white needles M.P. 254°C.

Analysis

C = 48.3%, H = 4.02%, N = 8.4%, I = 39.2% (found)

C = 48.2%, H = 4.01%, N = 8.6%, I = 39.2% (calculated).

Methiodide of 2-aza-carbazole was obtained as white needles M.P. 237°C.

Analysis

C - 46.2%, H - 3.5%, N - 8.8%, I - 41.0% (found)

C - 46.45%, H - 3.54%, N - 9.03%, I - 40.9% (calculated).

Anhydro salts from methiodide of aza-carbazole:-

The derivation of anhydro salt followed the same pattern. The pure methiodide was suspended in small quantity of water, and then treated with 2N. potassium carbonate solution. A yellow colour developed which was readily extracted into chloroform. The chloroform layer was dried over anhydrous sodium sulphate, and then concentrated to a small volume. Benzene was added to the concentrated solution. The solution on cooling yielded yellow crystals with excellent yields.

1-methyl-1-aza-carbazolium hydroxide anhydro salt crystallised as yellow rosettes M.P. 131-32°C.

Analysis.

C - 78.7%, H - 5.7%, N - 15.2%, (found)

C - 79.1%, H - 5.5%, N - 15.4%, (calculated).

2-methyl-2-aza-carbazolium hydroxide anhydro salt crystallises as yellow needles, M.P. 197-98°C.

Analysis.

C - 79.0%, H - 5.3%, N - 15% (found)

C - 79.1%, H - 5.5%, N - 15.4% (calculated).

Mono-nitration of aza-carbazole:- 10 gms. of desired aza-carbazole were suspended in 30 mls. of concentrated nitric acid in cold. The nitrate of the carbazole was immediately formed. 50 mls. of cold water were added, and the product was filtered. It was washed with 300 mls. of cold water, to remove excess of nitric acid. The solid was crystallised as a mono nitrate from ethanol, yielding 13.5 gms. of white needles of the nitrate. The product was dried in a steam oven. The dried product was gradually added to 150 mls. of concentrated sulphuric acid, keeping the temperature below 10°C. All the solid was added within about 30 minutes. It was warmed for 15 minutes over the water bath. An orange colour solution resulted. It was added to crushed pieces of ice and the diluted solution was neutralised with ammonia solution. The solid that separated was filtered, and crystallised with the suitable solvent.

Mono nitro-1-aza-carbazole:- The product came out as a pale yellow solid, which was crystallised from glacial acetic acid as pale yellow needles, which melted and immediately sublimed at 340°C. The

product readily sublimed at 210°C./1 mm. pressure. Yield 11 gms.

Analysis.

N = 20.3%, (found)

N = 19.7%, (calculated).

Mono nitro-2-aza-carbazole:- This was obtained as yellow solid, which was crystallised from acetone as yellow needles, M.P. 325-26°C.

Analysis

N = 20.0% (found)

N = 19.7% (calculated)

Methiodide of mono nitro-aza-carbazole:- Pure mono nitro aza-carbazole was suspended in analar acetone and was boiled under reflux, with excess of methyl iodide, when the solid methiodide separated. After two hours when the quarternisation was complete, excess of methyl iodide and acetone were distilled off and the residual solid was taken up in methanol, and crystallised.

Methiodide of mono-nitro-1-aza-carbazole:- It crystallised as yellow needles from methanol M.P. 345°C. (with charring). Good yield.

Analysis.

C = 40.8%, H = 2.8%, N = 12.1%, I = 36.2% (found)

C = 40.6%, H = 2.82%, N = 11.8%, I = 35.8% (calculated)

Methiodide of mono-nitro -2- aza-carbazole:- It crystallised as yellow orange needles from ethanol, and was

obtained in good yield. M.P. 256-57°C.

Analysis.

C = 40.3%, H = 2.75%, N = 11.3%, I = 35.5% (found)

C = 40.6%, H = 2.82%, N = 11.8%, I = 35.82% (calculated)

Derivation of the metho-betaine from the methiodide of mono-nitro-aza-carbazole:- The procedure followed for the preparation of the anhydro salt was the same as before. The recrystallised methiodide of mono-nitro-aza-carbazole was treated with 2N. potassium carbonate solution in cold. The yellow colour that was formed, was extracted into chloroform. The chloroform layer was dried over anhydrous potassium carbonate, and was concentrated to a small volume by distillation under low pressure. To the concentrated solution of the betaine in chloroform, benzene was added, while it was still hot. On cooling crystals of the betaine separated out, which were recrystallised from benzene chloroform mixture. The yield of the betaine was quantitative.

Metho-betaine of mono-nitro-1-aza-carbazole:- It crystallised out as yellow needles, M.P. 289-90°C.

Analysis.

C = 63.1%, H = 4.1%, N = 18.5% (found)

C = 63.4%, H = 4.0%, N = 18.5% (calculated).

Metho betaine of mono-nitro-2-aza-carbazole:- This crystallised out as orange yellow needles, M.P. 236-38°C.

Analysis

C = 63.2%, H = 4.2%, N = 18.7% (found)

C = 63.4%, H = 4.0%, N = 18.5% (calculated)

Reduction of mono-nitro-aza-carbazole to amino-aza-carbazole:- 5 gms. of recrystallised mono-nitro-aza-carbazole were suspended into 150 mls. of analar glacial acetic acid, placed in the hydrogenation flask. 5 mls. of the suspension of freshly prepared Raney Nickel in ethanol, were put into the flask. The reduction was carried out at the atmospheric pressure, and temperature 60°C. The temperature of the flask was maintained at 60°C. throughout the experiment with the help of an infra red radiator. Three moles were taken up during the experiment, when all the nitro compound went into the solution after reduction. The catalyst was separated by filtration and most of the solvent was distilled under reduced pressure. The residual solution was neutralised with sodium hydroxide solution. The solid that separated was filtered, washed with water, and dried. It was charcoaled in ethanol and was crystallised with suitable solvent.

Amino-1-aza-carbazole:- It crystallised as white needles from petrol benzene mixture. Yield 4 gms., M.P. (243-45°C).

Analysis

C = 71.5%, H = 5.1%, N = 22.1% (found)

C = 72.0%, H - 4.9%, N - 22.9% (calculated).

Amino-2-aza carbazole:- This crystallised as pale white needles from methanol-petrol mixture. Yield 3.8 gms., M.P. 268-72°C.

Analysis

C = 71.7%, H = 5.4%, N = 22.0% (found)

C = 72.0%, H = 4.9%, N = 22.9% (calculated)

Diazotisation of amino-aza-carbazole, and hydrolysis of the resulting diazo compound into phenol:-

3.5 gms. of amino-aza-carbazole, were dissolved in 150 mls. of 2N. sulphuric acid. This was cooled in an ice bath. A solution of 3 gms. of sodium nitrite in 10 mls. of water, was gradually added to the solution of the amino-aza-carbazole, with constant stirring. The temperature was kept below 0°C., during the addition of sodium nitrite solution. In half an hour the diazotisation was complete. The diazo compound was decomposed into phenol by heating the resultant mixture over the water bath for 24 hours, till the mixture did not give colour with alkaline β-naphthol. The solution was rendered neutral with sodium bicarbonate, and the solid that separated out was filtered and dried. This was extracted with ethyl acetate, with the help of a Soxhlet extractor. The yield of both hydroxy-aza-carbazoles was so poor, (hydroxy-1-aza-carbazole yield 500 mgs., hydroxy-2-aza-carbazole yield 300 mgs.) that they were converted into their methiodides, directly. The impure hydroxy-

aza-carbazole was dissolved in methanol and boiled with reflux with excess of methyl iodide for one hour, when the quarternisation was complete. Excess of methyl iodide and methanol were distilled and the residue was crystallised with methanol and ether.

Methiodide of hydroxy-1-aza-carbazole:- This crystallised out as pale yellow needles. M.P. 216°C.

Analysis.

C = 44.1%, H = 4.0%, N = 8.8%, I = 38.3%, (found)

C = 44.2%, H = 3.4%, N = 8.61%, I = 38.9%, (calculated).

Methiodide of hydroxy-2-aza-carbazole:- This crystallised out as pale yellow needles. M.P. 232°C.

Analysis.

C - 44.0%, H - 3.7%, N - 8.5%, I - 38.5% (found)

C - 44.2%, H - 3.4%, N - 8.6%, I - 38.9% (calculated).

Derivation of anhydro salt from the methiodide of hydroxy-aza-carbazole:- To a solution of methiodide of hydroxy-aza-carbazole in water, 2N. potassium carbonate was added. The yellow colour that was developed was extracted into chloroform. The chloroform layer was dried over anhydrous potassium carbonate, and then finally concentrated to a small volume, and the betaine was crystallised by addition of petrol.

Anhydro salt from methiodide of hydroxy-1-aza-carbazole:- This crystallised from petrol as yellow rosettes. M.P. 125°C.

Analysis.

N = 13.5% (found)

N = 14.1% (calculated).

The betaine on further boiling in analar acetone, with excess of methyl iodide, yielded another quarternary compound, recrystallised from ethanol and ether. M.P. 221°C.

Analysis.

N = 7.6%, I = 37% (found)

N = 8.2%, I = 37.4% (calculated).

Anhydro salt from the methiodide of hydroxy-2-aza-carbazole:- This was obtained in a very small quantity and could not be worked up for crystallisation.

Bromo-aza-carbazole:- This was obtained in two ways.

(1) Sandemeyer's reaction on amino-aza-carbazole

The amino compound was diazotised in 30 mls. of 40% hydrochromic acid solution, at 10°C. To this 1 gm. of freshly prepared cuprous bromide were added and then the solution was warmed over the water bath. There was immediate evolution of nitrogen. The warming was carried on for 2 hours. The solution was then extracted with chloroform in a separating funnel. The chloroform layer was dried over anhydrous sodium sulphate, filtered and then distilled off. The solid was taken up in benzene and chromatographed on alumina using benzene as eluent. The bromo compound was crystallised from suitable solvent. Yield 600 mgs.

(2) Direct bromination:- 3 gms. of carboline were dissolved in 50 mls. of glacial acetic acid. 2 mls. of bromine in 20 mls. of glacial acetic acid were dropped into the cold solution of the aza-carbazole. This was gently warmed over a water bath till a yellow solid began to separate. This was cooled and excess of bromine were removed with sodium sulphite solution. The solution was neutralised with dilute alkali, and the solid bromo compound that separated was filtered off. This was recrystallised from suitable solvents. The mixed melting point of the bromo compounds obtained by the two methods were undepressed in the case of both bromo-1-aza-carbazole, and bromo-2-aza-carbazole. The analysis did not agree with the required values, (probably due to the presence of some dibromo compound).

Bromo-1-aza-carbazole:- It was obtained as white crystalline needles from benzene. M.P. 268-70°C.

Analysis.

N = 10.5%, Br = 34% (found)

N = 11.3%, Br = 32.4% (calculated).

Bromo-2-aza-carbazole:- It was obtained as buff needles from methanol. M.P. 275°C.

Analysis.

N = 10.4%, Br = 35.6%, (found)

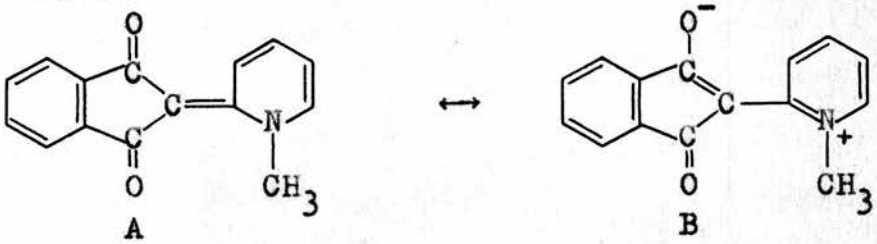
N = 11.3%, Br = 32.4%, (calculated)

SECTION (D)

Section D.

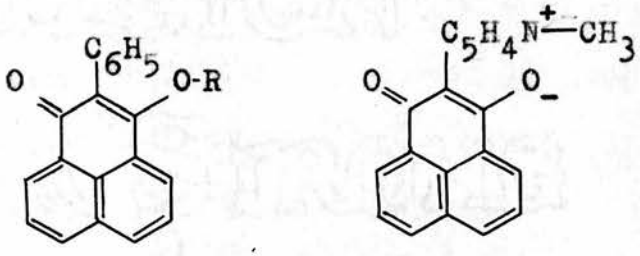
The pyrophthalones are postulated to be resonance hybrids involving anhydro-salt structures,

e.g. B.



A ↔ B

It was decided that reduction of such systems deserved study and derivatives of perinaphthindane were selected initially as the analogues containing phenyl rather than N-methylpyridinium substituents were available for comparative examination.

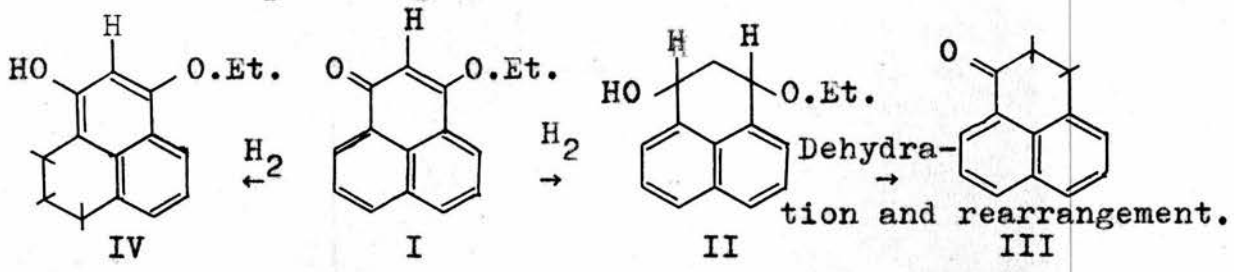


At the same time it was hoped to obtain passage from naphthindandiones to naphthindanones by hydrogenation. The work described is incomplete but serves as an introduction to a wider field.

(1) Studies on the reduction of the compounds in the perinaphthindane series:-

In attempting to synthesise perinaphthindanone III from 7:9-Diketoperi-naphthindane through the reduction of its ether I to the intermediate carbinol II and the subsequent dehydration and rearrangement to the desired compound III led to some interesting

results. The repeated attempts at reducing I with Li-AlH_4, Na/NH_3 and

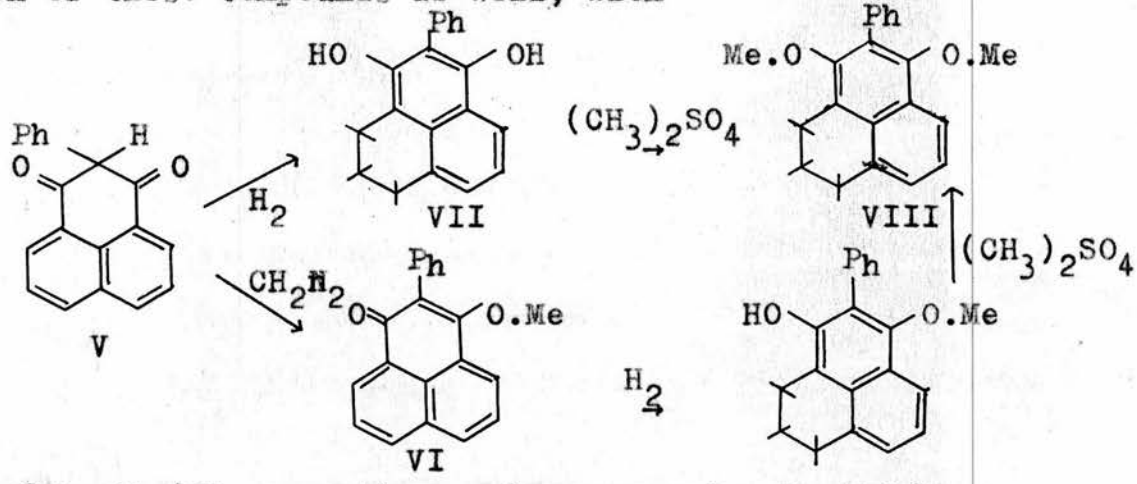


IV I II III

sodium amalgam met with no success, and the starting material was recovered back unchanged. Later on however the ether I was dissolved in glacial acetic acid and reduced catalytically with Adam's Catalyst at atmospheric pressure and room temperature. Two moles of hydrogen were taken up by the compound at a steady rate. The reaction product was crystallised from ethanol. The product which was expected to be the carbinol II, on treatment with the various dehydrating agents was unchanged. It was later on reported by M. Goldman (J. Amer. Chem. Soc., Aug. 1954, 4032) that the reduction went in the naphthalene nucleus, giving tetrahydronaphthalene structure IV to the resulting compound, which also explains the inertness of the compound towards the dehydrating agents to give desired perinaphthindanone. It was found that even with Raney nickel as catalyst (which is not effective in the reduction of the benzene rings) the reduction went in the naphthalene nucleus. The phenolic compound IV later, gave a diethoxy ether on further treatment with diethyl sulphate in

alkaline solution.

For comparative work 8-phenyl-7:9-diketo-perinaphthindane V, was prepared. Its treatment with diazomethane gave monomethyl ether VI. The reduction of these compounds as well, with



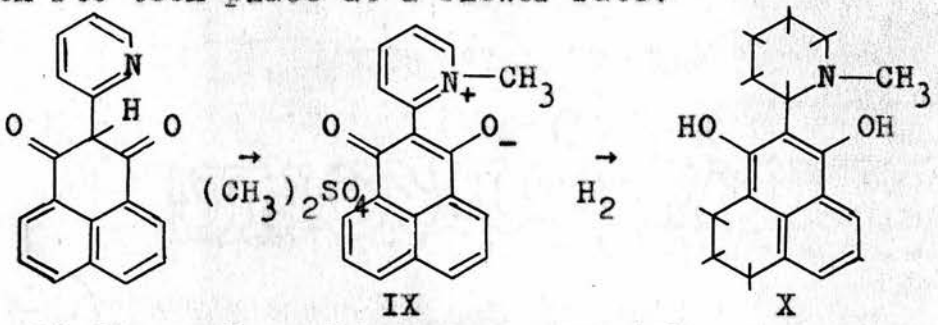
Li AlH_4, Na/NH_3 or sodium amalgam proved unfruitful. This compound could be reduced catalytically with Adam's Catalyst under identical conditions as I. In this case as well two moles of hydrogen were taken up. The resulting compound VII, gave a dimethoxy ether VIII, on methylation with dimethyl sulphate and, which corresponded with the dimethoxy ether of the reduction product of monomethyl ether VI.

The compound VII, was found to be unstable and decomposed on keeping in mother liquors into a yellow solid which did not correspond in its properties with the original compound and was not identified.

In these cases as well, the naphthalene nucleus is attacked. A diacetate of the phenol VII, was

made by acetylation with acetic anhydride.

Influence of pyridine ring instead of a benzene ring in the 8th position, did not have any marked effect in reduction as was found in the case of compound IX, obtained by the condensation of α-picoline with naphthalic anhydride (Eibner and Lobernig, Ber., 39, 2216) and its subsequent methylation with $(CH_3)_2 SO_4$. The catalytic reduction with PtO took place at a slower rate.



IX X

In all, five moles of hydrogen were taken up, presumably 2 moles by the naphthalene nucleus and then later 3 moles by the pyridine ring. The resulting product was acetylated, which crystallised and separated as colourless prisms.

Experimental

7:9-Diketoperinaphthindane:- This compound was prepared by malonic ester condensation with naphthalic anhydride (Errera Gazz., 1911, 41, 1) in presence of fused $ZnCl_2$. The product was crystallised from ethanol as yellow needles. M.P. 250-254°C. Yield recorded was 89% (unrecrystallised).

9-Ethoxy-perinaphthindenone:- 7:9-Diketo-perinaphthindane

was alkylated by esterifying it in alcoholic solution in presence of 5% concentrated sulphuric acid for 8 hours. The product was recrystallised as brownish yellow needles from petrol (80-100°) M.P. 148°C.

Reduction of 9-ethoxy-perinaphthindenone:- Repeated attempts for reduction of the compound with Li-AlH_4, Na/NH_3 or sodium amalgamet with no result.

4 gms. of 9-ethoxy-perinaphthindenone was dissolved in 150 mls. of glacial acetic acid. 200 mg. of Adam's Catalyst were added to this and the reduction was carried out at the atmospheric pressure and room temperature. Two moles of hydrogen were taken up by the compound at the rate of 20 mls. per five minutes. When the hydrogenation was complete, the catalyst was filtered off, and the acetic acid was removed by distillation under reduced pressure. Orange needles separated from the concentrated solution, which were recrystallised from ethanol after charcoaling. The product on recrystallising weighed 3.9 gms. Further purification could be achieved by sublimation at 150°C/2 mm. pressure.

Analysis

(found) C = 79.2%, H = 7.2%

(calculated) C = 79.0%, H = 7.0%

From treatment of this compound with cold $CnnH_2SO_4$

or syrupy H_3PO_4 or refluxing with formic acid, the unchanged material was recovered back showing thereby that the reduction went in the naphthalene nucleus.

Alkylation of 9-ethoxy perinaphthindane:- 3 gms. of 9-ethoxy-perinaphthane were dissolved in 150 mls. of 2N. NaoH solution with the help a few mls. dioxan. This was kept refluxing in a round bottomed flask for 2 hours with 1½ moles of diethyl sulphate run into it gradually drop by drop. The solution was kept alkaline throughout by the addition of more N/10 NaOH solution. This was then cooled and extracted with ether. The ether layer was dried over anhydrous Na_2SO_4 and then distilled off. The residue was taken up in benzene and chromatographed over alumina, using benzene as eluent. The product was crystallised from benzene and petrol (80-100°C.) as white needles. M.P. 93°C. Yield 2.3 gms.

Analysis

(found) C = 79.8%, H = 8.1%

(calculated) C = 79.7%, H = 7.8%

8-phenyl-7:9-diketo-perinaphthindane:- Reduction of the well known 8-phenyl-7:9-diketo-perinaphthindane (prepared by Mr. L. Morrison) was tried with Li-AlH_4 Na/NH_3 and sodium amalgam, which again did not yield any result.

4 gms. of 8-phenyl-7:9-diketo-perinaphthindane were suspended in 150 mls. of analar. glacial acetic

acid. To this 200 mgs. of platinum oxide were added and the compound was reduced catalytically at room temperature and atmospheric pressure. Two moles of hydrogen were taken up during the process of reduction at the rate of 35 mls. per five minutes. The catalyst was filtered and all glacial acetic acid was distilled off under reduced pressure. The remainder was taken up in chloroform and the chloroform layer was washed with alkali and finally with water. This was dried over anhydrous sodium sulphate. Chloroform was then distilled off. The remaining oil was taken up in benzene and charcoaled. Large light orange lumps of the product VII separated with difficulty on addition of petrol (60-80°C). Yield 2.5 gms. M.P. 99-100°C.

Analysis

(found) C = 82.2% H = 5.43%

(calculated) C = 82.6% H = 5.8%

The mother liquors left after the crystallisation of the above compound, after a week, left behind a yellow solid, which was insoluble in benzene and was crystallised with ethyl acetate, as yellow prisms. M.P. 180°C.

Analysis C = 76.65% H = 5.63%

Methylation of 1:3-dihydroxy-2-phenyl-perinaphthindane VII:-

1.3 gms. of 1:3-dihydroxy-2-phenyl-perinaphthindane

was dissolved in 100 mls. of $\frac{N}{10}$ NaoH, with the addition of 2 mls. of dioxan . This was kept refluxing for 1 hour, with the dropwise addition of 5 mls. of dimethyl sulphate. The solution was kept alkaline at the end of the reaction, and later was extracted with ether. The ether layer was dried over anhydrous sodium sulphate. Ether was then distilled off leaving behind an oil which was taken up in benzene and chromatographed on alumina, using benzene as eluent. A pale yellow band separated which fluoresced blue in ultra violet light. Benzene was distilled off and the straw coloured oil was crystallised as white needles, with light petrol (40-60°C.) yield 1 gm. M.P. 80-82°C.

Analysis.

(found) C = 82.54% H = 6.1%

(calculated) C = 82.9% H = 6.6%

Acetylation of 1:3-dihydroxy-2-phenyl-perinaphthindane VII:-

2.8 gms. of 1:3-dihydroxy-2-phenyl-perinaphthindane were dissolved in 5 mls. of glacial acetic acid, and then 3 mls. of acetic anhydride were added followed by a drop of concentrated sulphuric acid. Heat was liberated on addition of sulphuric acid. The solution was warmed on a water bath and then cooled after three minutes. 10 gms. of crushed

pieces of ice were added to it. A white solid separated out on further addition of water. Filtration of the solid and recrystallisation gave white needles from glacial acetic acid. Yield 2.3 gms. M.P. 194-195°C.

Analysis.

(found) C = 76.7% H = 4.74%

(calculated) C = 76.9% H = 5.6%

Preparation of 8-phenyl-9-methoxy-perinaphthindenone VI:-

2 gms.of 8-phenyl-7:9-diketoperinaphthindane were suspended in dry ethereal solution of freshly prepared diazomethane, liberated from 5 gms.of N-nitroso N-methyl urea. The solid gradually went into the solution with the evolution of nitrogen bubbles, the colour of the solution turning from yellow to orange. This was left overnight. Next day all the solid went into ether, This was filtered and ether was distilled off. The solid left behind was crystallised from petrol (80-100°C) as yellow needles. M.P. 110°C. Yield = 2.1 gms.(pure compound).

Analysis.

(found) C = 83.4% H = 4.9%

(calculated) C = 83.9% H = 4.9%

Reduction of 8-phenyl-9-methoxyperinaphthindenone: VII:-

Reduction of this compound, as before was

carried out catalytically. 1.1 gms. of the 8-phenyl-9-methoxyperinaphthindenone were dissolved in 50 mls. of analar glacial acetic acid. To this 50 mgs. of Adam's Catalyst were added, and then reduced at room temperature and atmospheric pressure. Two moles of hydrogen were taken up during the process of reduction. The catalyst was separated by filtration and the glacial acetic acid was distilled off under reduced pressure. The oil that was left behind was dissolved in 100 mls. of N/10 NaoH with the help of 2 mls. of dioxan and was methylated by the addition of 5 mls. of dimethyl sulphate, keeping the solution refluxing for one hour. The final alkaline solution was extracted in the ether and then chromatographed on alumina using benzene as eluent. A blue fluorescent band under ultra violet light, separated. The benzene was distilled off and the product was crystallised as white needles from (40-60°) petrol. M.P. 80-82° C. Yield 0.8 gms. The mixed melting point of the compound was undepressed with 1:3-dimethoxy-2-phenyl-peri-naphthindane, obtained by other method described before.

8÷ (N-methyl pyridinium)-7:9÷diketo-perinaphthindane:-

8-pyridyl-7:9-diketoperinaphthindane (Eibner and Lobernig, Ber., 39, 2216) was obtained as crystalline

yellow solid by the condensation of picoline with naphthalic anhydride. 6 gms. of this compound was dissolved in 2 moles of N/10 NaoH and refluxed for 4 hours with the gradual addition of 1½ moles of dimethyl sulphate. The resultant alkaline solution was extracted with ether. The ether layer was dried over anhydrous sodium sulphate and then distilled. The residue was taken in benzene and chromatographed on alumina, using benzene as eluent. The yellow band that separated crystallised as yellow needles from petrol and benzene. M.P. 230°C. Yield 5.3 gms.

2 gms. of the above compound were dissolved in 50 mls. of analar glacial acetic acid, and reduced catalytically with 50 mgs. of PtO. The intake of hydrogen was comparatively slower than in the previous experiments. In all 5 moles of hydrogen were taken up. The catalyst was filtered off, and acetic acid was removed by distillation under reduced pressure. The residual oil was taken in 5 mls. of acetic anhydride followed by the addition of a drop of Con. H_2SO_4. After three minutes of gentle warming, crushed ice was added to it, and finally basified with dil. NaoH solution. The alkaline solution was extracted with ether. The ethereal layer after drying over anhydrous sodium sulphate was distilled off. The oil that remained was

chromatographed on alumina, in benzene. A fluorescent band under the ultra violet light separated which was eluted with petrol (40-60°C). From this the product crystallised as colourless prisms after several days. M.P. 75°C. Yield 500 mgs.

Analysis of the diacetyl compound of X. C = 71.9% H = 6.8% N = 2.9% (found)
C = 72.4% H = 7.09% N = 3.68% (calculated)

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